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JP**(54) DIELECTRIC CERAMIC COMPOSITION, ELECTRONIC COMPONENT AND METHOD OF MANUFACTURING ELECTRONIC COMPONENT****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a dielectric ceramic composition excellent in reduction resistance at baking, having good capacitance temperature characteristics after firing and capable of improving acceleration life of insulation resistance.

**SOLUTION:** The dielectric ceramic composition has a main ingredient containing dielectric oxide of composition represented by  $[(\text{Sr}_{1-x}\text{Ca}_x)\text{O}]_m(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_2$  and at least a first sub ingredient containing  $\geq$  one kinds selected from among oxides of V, Nb, W, Ta and Mo and/or compounds becoming these oxides after firing, and the marks m, x, and y show composing mole ratios in the formula of main ingredient, have relations of  $0.94 < m < 1.08$ ,  $0 \leq x \leq 1.00$ ,  $0 \leq y \leq 0.20$ , and the ratio of the main ingredient of 100 mol to the first sub ingredient is  $0.01 \text{ mol} \leq$  the first sub ingredient  $\leq 2 \text{ mol}$  in terms of metallic element in the oxide.

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(54) 【発明の名称】 誘電体磁器組成物、電子部品および電子部品の製造方法

## (57) 【要約】

【課題】 焼成時の耐還元性に優れ、焼成後には優れた容量温度特性を有し、しかも絶縁抵抗の加速寿命を向上させることができる誘電体磁器組成物を提供する。

【解決手段】  $\{(\text{Sr}_{1-x}\text{Ca}_x)\text{O}\}_m \cdot (\text{Ti}_{1-y}\text{Zr}_y)\text{O}_2$  で示される組成の誘電体酸化物を含む主成分と、V、Nb、W、TaおよびMoの酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む第1副成分とを少なくとも有する誘電体磁器組成物であって、前記主成分に含まれる式中の組成モル比を示す記号m、xおよびyが、 $0.94 < m < 1.08$ 、 $0 \leq x \leq 1.00$ 、 $0 \leq y \leq 0.20$ の関係にあり、前記主成分100モルに対する前記第1副成分の比率が、酸化物中の金属元素換算で、 $0.01 \text{モル} \leq \text{第1副成分} < 2 \text{モル}$ である。

## 【特許請求の範囲】

【請求項 1】  $\{ (Sr_{1-x}Ca_x)O \}_m \cdot (Ti_{1-y}Zr_y)O_2$  で示される組成の誘電体酸化物を含む主成分と、

V、Nb、W、Ta および Mo の酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる 1 種類以上を含む第 1 副成分とを少なくとも有する誘電体磁器組成物であって、

前記主成分に含まれる式中の組成モル比を示す記号 m、x および y が、

$0.94 < m < 1.08$ 、

$0 \leq x \leq 1.00$ 、

$0 \leq y \leq 0.20$  の関係にあり、

前記主成分 100 モルに対する前記第 1 副成分の比率が、酸化物中の金属元素換算で、 $0.01 \text{ モル} \leq \text{第 1 副成分} < 2 \text{ モル}$  である誘電体磁器組成物。

【請求項 2】 Mn の酸化物および／または焼成により Mn の酸化物になる化合物を含む第 2 副成分をさらに有し、

前記主成分 100 モルに対する前記第 2 副成分の比率が、酸化物中の金属元素換算で、 $0 \text{ モル} \leq \text{第 2 副成分} < 4 \text{ モル}$  である請求項 1 記載の誘電体磁器組成物。

【請求項 3】  $SiO_2$ 、MO（ただし、M は、Ba、Ca、Sr および Mg から選ばれる少なくとも 1 種の元素）、 $Li_2O$  および  $B_2O_3$  から選ばれる少なくとも 1 種を含む第 3 副成分をさらに有し、

前記主成分 100 モルに対する前記第 3 副成分の比率が、酸化物換算で、 $0 \text{ モル} < \text{第 3 副成分} < 15 \text{ モル}$  である請求項 1 または 2 記載の誘電体磁器組成物。

【請求項 4】  $(Sr_p, Ca_{1-p})SiO_3$ （ただし、p は  $0.3 \leq p \leq 1$ ）を含む第 3 副成分をさらに有し、

前記主成分 100 モルに対する前記第 3 副成分の比率が、酸化物換算で、 $0 \text{ モル} < \text{第 3 副成分} < 15 \text{ モル}$  である請求項 1 または 2 記載の誘電体磁器組成物。

【請求項 5】 温度に対する静電容量変化率 ( $\Delta C$ ) が、少なくとも  $20 \sim 85^\circ\text{C}$  の温度範囲内において、 $-2000 \sim 0 \text{ ppm}/^\circ\text{C}$ （ただし、静電容量 C の基準温度は  $20^\circ\text{C}$ ）である請求項 1～4 の何れかに記載の誘電体磁器組成物。

【請求項 6】 誘電体層を有する電子部品であって、前記誘電体層が、誘電体磁器組成物で構成してあり、前記誘電体磁器組成物が、 $\{ (Sr_{1-x}Ca_x)O \}_m \cdot (Ti_{1-y}Zr_y)O_2$  で示される組成の誘電体酸化物を含む主成分と、

V、Nb、W、Ta および Mo の酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる 1 種類以上を含む第 1 副成分とを少なくとも有し、

前記主成分に含まれる式中の組成モル比を示す記号 m、x および y が、

$0.94 < m < 1.08$ 、

$0 \leq x \leq 1.00$ 、

$0 \leq y \leq 0.20$  の関係にあり、

前記主成分 100 モルに対する前記第 1 副成分の比率が、酸化物中の金属元素換算で、 $0.01 \text{ モル} \leq \text{第 1 副成分} < 2 \text{ モル}$  である電子部品。

【請求項 7】 前記誘電体層と共に内部電極層とが交互に積層してあるコンデンサ素子本体を有する請求項 6 記載の電子部品。

10 【請求項 8】 前記内部電極層に含まれる導電材がニッケルまたはニッケル合金である請求項 7 記載の電子部品。

【請求項 9】  $\{ (Sr_{1-x}Ca_x)O \}_m \cdot (Ti_{1-y}Zr_y)O_2$  で示される組成の誘電体酸化物を含む主成分と、

V、Nb、W、Ta および Mo の酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる 1 種類以上を含む第 1 副成分とを少なくとも有し、

前記主成分に含まれる式中の組成モル比を示す記号 m、x および y が、

$0.94 < m < 1.08$ 、

$0 \leq x \leq 1.00$ 、

$0 \leq y \leq 0.20$  の関係にあり、

前記主成分 100 モルに対する前記第 1 副成分の比率が、酸化物中の金属元素換算で、 $0.01 \text{ モル} \leq \text{第 1 副成分} < 2 \text{ モル}$  である誘電体磁器組成物を用いて誘電体ペーストを作製する工程と、

内部電極用ペーストを作製する工程と、

前記誘電体ペーストおよび内部電極用ペーストを交互に

30 積層して積層体を得る工程と、

前記積層体を焼成して焼結体を得る焼成工程と、前記焼結体を、酸素分圧が  $10^{-4}$  Pa 以上の雰囲気下で熱処理する工程とを有する電子部品の製造方法。

【請求項 10】 前記焼成工程において、前記積層体を、酸素分圧が  $10^{-10} \sim 10^{-3}$  Pa の雰囲気下で焼成する請求項 9 記載の電子部品の製造方法。

【請求項 11】 前記内部電極用ペーストとして、ニッケルまたはニッケル合金を用いる請求項 9 または 10 記載の電子部品の製造方法。

40 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、たとえば積層型セラミックコンデンサの誘電体層などとして用いられる誘電体磁器組成物と、その誘電体磁器組成物を誘電体層として用いる電子部品およびその製造方法に関する。

【0002】

【従来の技術】電子部品の一例である積層型セラミックコンデンサは、所定の誘電体磁器組成物からなるグリーンシート上に導電ペーストを印刷し、該導電ペーストを印刷した複数枚のグリーンシートを積層し、グリーンシ

ートと内部電極とを一体的に焼成し、形成されている。

【0003】従来の誘電体磁器組成物は、低酸素分圧である中性または還元性雰囲気下で焼成すると還元され、半導体化する性質を有していた。このため、積層型セラミックコンデンサを製造するに際しては、高酸素分圧である酸化性雰囲気下で焼成することを余儀なくされていた。これに伴い、誘電体磁器組成物と同時に焼成される内部電極材料としては、該誘電体磁器組成物が焼結する温度で熔融せず、酸化性雰囲気下で焼成しても酸化されない高価な貴金属（たとえばパラジウムや白金など）を用いる必要があり、製造される積層型セラミックコンデンサの低価格化に対して大きな妨げとなっていた。

【0004】これに対して、安価な卑金属（たとえばニッケルや銅など）を内部電極の材料として用いるためには、中性または還元性雰囲気下において低温で焼成しても半導体化せず、すなわち耐還元性に優れ、焼成後には十分な比誘電率と優れた誘電特性（たとえば容量温度変化率が小さいなど）とを有する誘電体磁器組成物を開発することが必要である。

【0005】従来、内部電極の材料として卑金属を用いることができる誘電体磁器組成物として種々の提案がなされている。

【0006】たとえば、特開昭63-224108号公報では、 $(\text{Sr}_{1-x}\text{Ca}_x)_m(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$  で示される組成の誘電体酸化物（ただし、 $0.30 \leq x \leq 0.50$ 、 $0.03 \leq y \leq 0.20$ 、 $0.95 \leq m \leq 1.08$ ）を主成分とし、この主成分100重量部に対して、副成分として、Mnを $\text{MnO}_2$  換算で0.01~2.00重量部、 $\text{SiO}_2$  を0.10~4.00重量部含有する誘電体磁器組成物が開示してある。

【0007】また、特開昭63-224109号公報では、前記主成分に対し、前記Mnおよび $\text{SiO}_2$  に加えて、さらに $\text{ZnO}$ を0.01~1.00重量部含有する誘電体磁器組成物が開示してある。

【0008】さらに、特開平4-206109号公報では、 $(\text{Sr}_{1-x}\text{Ca}_x)_m(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$  で示される組成の誘電体酸化物（ただし、 $0.30 \leq x \leq 0.50$ 、 $0.00 \leq y \leq 0.20$ 、 $0.95 \leq m \leq 1.08$ ）を主成分とし、その粉末粒径を0.1~1.0 $\mu\text{m}$ の範囲にしてある誘電体磁器組成物が開示してある。

【0009】さらにまた、特公昭62-24388号公報では、 $(\text{MeO})_k\text{TiO}_2$  で示される組成の誘電体酸化物（ただし、MeはSr、Caおよび $\text{Sr}+\text{Ca}$ から選択された金属、kは1.00~1.04）を主成分とし、この主成分100重量部に対して、ガラス成分として、 $\text{Li}_2\text{O}$ 、M（ただし、Mは $\text{BaO}$ 、 $\text{CaO}$ および $\text{SrO}$ から選択される少なくとも1種の金属酸化物）および $\text{SiO}_2$ を所定のモル比で用いたものを0.

2~10.0重量部含有する誘電体磁器組成物が開示してある。

【0010】

【発明が解決しようとする課題】しかしながら、これらの公報記載の誘電体磁器組成物では、何れも焼成後の絶縁抵抗の加速寿命が短く、該誘電体磁器組成物を用いてニッケルなどの卑金属製内部電極を有する積層型セラミックコンデンサを製造した場合には得られる積層型セラミックコンデンサの信頼性が低くなるといった問題があった。

【0011】本発明の目的は、焼成時の耐還元性に優れ、焼成後には優れた容量温度特性を有し、しかも絶縁抵抗の加速寿命を向上させることができる誘電体磁器組成物を提供することにある。また本発明の目的は、優れた容量温度特性を有し、しかも絶縁抵抗の加速寿命が向上され、信頼性が高められたチップコンデンサなどの電子部品を提供することである。さらに本発明の目的は、電子部品に求められる信頼性を維持しながら、初期絶縁抵抗の不良率の発生を改善できる電子部品の製造方法を提供することである。

【0012】

【課題を解決するための手段】上記目的を達成するために、本発明に係る誘電体磁器組成物は、 $\{(\text{Sr}_{1-x}\text{Ca}_x)\text{O}\}_m \cdot (\text{Ti}_{1-y}\text{Zr}_y)\text{O}_2$  で示される組成の誘電体酸化物を含む主成分と、V、Nb、W、TaおよびMoの酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む第1副成分とを少なくとも有する誘電体磁器組成物であって、前記主成分に含まれる式中の組成モル比を示す記号m、xおよびyが、

$0.94 < m < 1.08$ 、

$0 \leq x \leq 1.00$ 、

$0 \leq y \leq 0.20$ の関係にあり、

前記主成分100モルに対する前記第1副成分の比率が、酸化物中の金属元素換算で、 $0.01 \text{モル} \leq \text{第1副成分} < 2 \text{モル}$ であることを特徴とする。

【0013】好ましくは、本発明に係る誘電体磁器組成物は、Mnの酸化物および／または焼成によりMnの酸化物になる化合物を含む第2副成分をさらに有し、前記主成分100モルに対する前記第2副成分の比率が、酸化物中の金属元素換算で、 $0 \text{モル} \leq \text{第2副成分} < 4 \text{モル}$ である。

【0014】好ましくは、本発明に係る誘電体磁器組成物は、 $\text{SiO}_2$ 、 $\text{MO}$ （ただし、Mは、Ba、Ca、SrおよびMgから選ばれる少なくとも1種の元素）、 $\text{Li}_2\text{O}$ および $\text{B}_2\text{O}_3$ から選ばれる少なくとも1種を含む第3副成分をさらに有し、前記主成分100モルに対する前記第3副成分の比率が、酸化物換算で、 $0 \text{モル} < \text{第3副成分} < 15 \text{モル}$ である。第3副成分は、焼結助剤として機能すると考えられる。

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【0015】第3副成分の特に好ましい態様は、以下に示すとおりである。より好ましくは、本発明に係る誘電体磁器組成物は、 $(\text{Sr}_{1-p}, \text{Ca}_{1-p})\text{SiO}_3$

(ただし、 $p$ は $0.3 \leq p \leq 1$ )を含む第3副成分をさらに有し、前記主成分100モルに対する前記第3副成分の比率が、酸化物換算で、 $0 \text{モル} < \text{第3副成分} < 15 \text{モル}$ である。この種の第3副成分は、焼結助剤として機能すると考えられる。

【0016】好ましくは、本発明に係る誘電体磁器組成物は、温度に対する静電容量変化率( $\Delta C$ )が、少なくとも $20 \sim 85^\circ\text{C}$ の温度範囲内において、 $-2000 \sim 0 \text{ppm}/^\circ\text{C}$ 、好ましくは $-1500 \sim 0 \text{ppm}/^\circ\text{C}$ 、より好ましくは $-1000 \sim 0 \text{ppm}/^\circ\text{C}$ である。ただし、静電容量 $C$ の基準温度は $20^\circ\text{C}$ である。

【0017】上記目的を達成するために、本発明に係る電子部品は、誘電体層を有する電子部品であって、前記誘電体層が、上記いずれかの誘電体磁器組成物で構成してあることを特徴とする。

【0018】好ましくは、本発明に係る電子部品は、前記誘電体層と共に内部電極層とが交互に積層してあるコンデンサ素子本体を有する。

【0019】好ましくは、本発明に係る電子部品は、前記内部電極層に含まれる導電材がニッケルまたはニッケル合金である。

【0020】上記目的を達成するために、本発明に係る電子部品の製造方法は、上記いずれかの誘電体磁器組成物を用いて誘電体ペーストを作製する工程と、内部電極用ペーストを作製する工程と、前記誘電体ペーストおよび内部電極用ペーストを交互に積層して積層体を得る工程と、前記積層体を焼成して焼結体を得る焼成工程と、前記焼結体を、酸素分圧が $10^{-4} \text{Pa}$ 以上、好ましくは $10^{-1} \sim 10 \text{Pa}$ の雰囲気下で熱処理する工程とを有する。

【0021】好ましくは、本発明に係る電子部品の製造方法は、前記焼成工程において、前記積層体を、酸素分圧が $10^{-10} \sim 10^{-3} \text{Pa}$ の雰囲気下で焼成する。

【0022】好ましくは、本発明に係る電子部品の製造方法は、前記内部電極用ペーストとして、ニッケルまたはニッケル合金を用いる。なお、本発明に係る誘電体磁器組成物において、第3副成分に含有される $\text{SiO}_2$ 、 $\text{MO}$ 、 $\text{Li}_2\text{O}$ 、 $\text{B}_2\text{O}_3$ および $(\text{Sr}_{1-p}, \text{Ca}_{1-p})\text{SiO}_3$ のそれぞれは、少なくとも焼成後にこうした組成になっていけばよい趣旨であり、焼成後にこれらの酸化物になる化合物を含む。

【0023】

【作用】本発明に係る誘電体磁器組成物では、特定組成の誘電体酸化物を含む主成分に対して、特定の第1副成分を所定量添加することにより、焼成時の耐還元性に優れ、焼成後には優れた容量温度特性を有するとともに、

第1副成分を添加しない場合に比べて、絶縁抵抗の加速寿命が1000倍(たとえば $175^\circ\text{C}$ 、 $\text{DC } 8 \text{V}/\mu\text{m}$ )以上に向上する。

【0024】本発明に係るチップコンデンサなどの電子部品では、本発明に係る誘電体磁器組成物で構成してある誘電体層を有するので、優れた容量温度特性(たとえばJIS規格のSL特性を満足する)を有し、しかも絶縁抵抗の加速寿命が向上され、電子部品の信頼性が向上する。

【0025】本発明に係る電子部品の製造方法では、焼成により得られる焼結体を酸素分圧が $10^{-4} \text{Pa}$ 以上の雰囲気下で熱処理する工程を有することにより、チップコンデンサなどの電子部品に求められる信頼性を維持しながら、初期絶縁抵抗の不良率の発生を効率的に改善することができる。

【0026】

【発明の実施の形態】以下、本発明を、図面に示す実施形態に基づき説明する。図1は本発明の一実施形態に係る積層セラミックコンデンサの断面図、図2は本発明の実施例である試料4の容量温度特性を示すグラフ、図3は本発明の実施例である試料3、4における $V$ の添加量と高温負荷寿命時間との関係を示すグラフ、図4は本発明の実施例である試料9～11における $V$ の添加量と高温負荷寿命時間との関係を示すグラフ、図5は本発明の実施例である試料19、20の容量温度特性を示すグラフ、図6は第3副成分の種類を代えたときの、誘電体層の厚みと初期絶縁抵抗との関係を示すグラフ、図7は誘電体層の厚みを代えたときに、 $\text{Li}$ 添加の有無と初期絶縁抵抗の不良率との関係を示すグラフ、図8は第4副成分としての $V$ の添加の有無と、高温負荷寿命との関係を示すグラフ、図9は誘電体層の厚みを代えたときに、熱処理工程における酸素分圧と初期絶縁抵抗の不良率との関係を示すグラフ、図10は第3副成分としての $(\text{Sr}_{1-p}, \text{Ca}_{1-p})\text{SiO}_3$ において $\text{Sr}$ の含有割合と、コンデンササンプルの初期絶縁抵抗( $\text{IR}$ )の良品率との関係を示すグラフである。

【0027】積層セラミックコンデンサ

図1に示すように、本発明の一実施形態に係る電子部品としての積層セラミックコンデンサ1は、誘電体層2と内部電極層3とが交互に積層された構成のコンデンサ素子本体10を有する。このコンデンサ素子本体10の両端部には、素子本体10の内部で交互に配置された内部電極層3と各々導通する一対の外部電極4が形成してある。コンデンサ素子本体10の形状に特に制限はないが、通常、直方体状とされる。また、その寸法にも特に制限はなく、用途に応じて適当な寸法とすればよいが、通常、 $(0.6 \sim 5.6 \text{mm}) \times (0.3 \sim 5.0 \text{mm}) \times (0.3 \sim 1.9 \text{mm})$ 程度である。内部電極層3は、各端面がコンデンサ素子本体10の対向する2端部の表面に交互に露出するように積層してある。一対の

外部電極4は、コンデンサ素子本体10の両端部に形成され、交互に配置された内部電極層3の露出端面に接続されて、コンデンサ回路を構成する。

#### 【0028】誘電体層2

誘電体層2は、本発明の誘電体磁器組成物を含有する。本発明の誘電体磁器組成物は、 $\{(Sr_{1-x}Ca_x)O\}_m \cdot (Ti_{1-y}Zr_y)O_2$  で示される組成の誘電体酸化物を含む主成分と、V、Nb、W、TaおよびMoの酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む第1副成分とを少なくとも含有する。この際、酸素(O)量は、上記式の化学量論組成から若干偏倚してもよい。

【0029】上記式中、xは、 $0 \leq x \leq 1.00$ 、好ましくは $0.30 \leq x \leq 0.50$ である。xはCa原子数を表し、x、すなわちCa/Sr比を変えることで結晶の相転移点を任意にシフトさせることが可能となる。そのため、容量温度係数や比誘電率を任意に制御することができる。xを上記範囲とすると、結晶の相転移点が室温付近に存在し、静電容量の温度特性を向上させることができる。ただし、本発明においては、SrとCaとの比率は任意であり、一方だけを含有するものであってもよい。

【0030】上記式中、yは、 $0 \leq y \leq 0.20$ 、好ましくは $0 \leq y \leq 0.10$ である。yを0.20以下とすることにより比誘電率の低下が防止される。yはZr原子数を表すが、 $TiO_2$  に比べ還元されにくい $ZrO_2$  を置換していくことにより耐還元性がさらに増していく傾向がある。ただし、本発明においては、必ずしもZrを含まなくてもよく、Tiだけを含有するものであってもよい。

【0031】上記式中、mは、 $0.94 < m < 1.08$ 、好ましくは $0.970 \leq m \leq 1.030$ である。mを0.94より大きくすることにより還元雰囲気下での焼成に対して半導体化を生じることが防止され、mを1.08未満にすることにより焼成温度を高くしなくても緻密な焼結体を得ることができる。

【0032】本発明の誘電体磁器組成物が、従来の誘電体磁器組成物と異なる点は、mが $0.94 < m < 1.08$ の範囲で、所定の第1副成分を所定量添加する点にある。所定の第1副成分を所定量添加することにより、主成分のmが $0.94 < m < 1.08$ の範囲での誘電特性を劣化させることなく低温焼成が可能となり、誘電体層を薄層化した場合でも絶縁抵抗の加速寿命(高温負荷寿命)を向上でき、信頼性を大幅に向上できる。その結果、コンデンサの小型化・高容量化が可能となる。

【0033】本発明では、第1副成分は、V、Nb、W、TaおよびMoの酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を少なくとも含む。この第1副成分は、焼結温度を低下させ

るとともに、絶縁抵抗の加速寿命を向上させる物質として作用する。本発明では、主成分100モルに対する第1副成分の比率は、酸化物中の金属元素換算で、 $0.01 \text{モル} \leq \text{第1副成分} < 2 \text{モル}$ 、好ましくは $0.04 \text{モル} \leq \text{第1副成分} \leq 0.6 \text{モル}$ である。第1副成分の比率を、酸化物中の金属元素換算で、 $0.01 \text{モル} \leq \text{第1副成分} < 2 \text{モル}$ の範囲にすることにより、mが $0.94 < m < 1.08$ の範囲において絶縁抵抗の加速寿命を向上できる。好ましくは、第1副成分として、Vの酸化物および／または焼成によりVの酸化物になる化合物を、V換算で、 $0.01 \text{モル}$ 以上2モル未満、好ましくは $0.04 \text{モル}$ 以上 $0.6 \text{モル}$ 以下程度含有させる。こうした特定の第1副成分を上記範囲で含有させることにより、高温負荷寿命の向上に効果的である。

【0034】また、本発明に係る誘電体磁器組成物では、Mnの酸化物(たとえば $MnO$ )および／または焼成によりMnの酸化物になる化合物(たとえば $MnCO_3$ )を含む第2副成分がさらに添加してあることが好ましい。この第2副成分は、焼結を促進する効果と高温負荷寿命を改善する効果を有し、しかも誘電体層2をたとえば $4 \mu m$ 程度に薄層化したときの初期絶縁抵抗(IR)不良率を低下させる効果も有する。前記主成分100モルに対する第2副成分の比率は、酸化物中の金属元素換算で、 $0 \text{モル} \leq \text{第2副成分} < 4 \text{モル}$ 、好ましくは $0.05 \text{モル} \leq \text{第2副成分} \leq 1.4 \text{モル}$ である。第2副成分の添加量が4モル以上であると、初期絶縁抵抗がとれない傾向があり、第2副成分の添加量が $0 \text{モル} \leq \text{第2副成分} < 4 \text{モル}$ の範囲では、添加量が多いほど、高温負荷寿命が向上され、しかも初期IR不良率の発生を低減でき、添加量が少ないほど、容量温度変化率を小さくできる。

【0035】さらに、本発明に係る誘電体磁器組成物では、 $SiO_2$ 、MO(ただし、Mは、Ba、Ca、SrおよびMgから選ばれる少なくとも1種の元素)、 $Li_2O$ および $B_2O_3$ から選ばれる少なくとも1種を含む第3副成分がさらに添加してあることが好ましい。この第3副成分は、主として焼結助剤として作用するが、薄層化した際の初期絶縁抵抗(IR)の不良率を改善する効果をも有する。不良率改善の観点からは、 $Li_2O$ を含有させることがより好ましい。また、不良率改善の観点からは、 $(Sr_p, Ca_{1-p})SiO_3$ を含有させることがより好ましい。この場合において、pは、 $0.3 \leq p \leq 1$ 、好ましくは $0.5 \leq p \leq 1$ である。pはSr原子数を表すが、このpの値を増加させることにより、初期IRの良品率を向上させることが可能となる。

【0036】前記主成分100モルに対する前記第3副成分の比率は、酸化物換算で、 $0 \text{モル} < \text{第3副成分} < 15 \text{モル}$ 、好ましくは $0.2 \text{モル} \leq \text{第3副成分} \leq 6 \text{モル}$ である。第3副成分の添加量を0モルより多くすることに

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より、焼結性の改善に効果的であり、添加量を 15 モル未満とすることにより、比誘電率の低下を抑え、十分な容量を確保できる。

【0037】さらにまた、本発明に係る誘電体磁器組成物には、R の酸化物（ただし、R は、Sc、Y、La、Ce、Pr、Nd、Pm、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm、Yb および Lu の少なくとも一つの元素）を含む第 4 副成分がさらに添加してあることが好ましい。この第 4 副成分は、高温負荷寿命を改善する効果の他、薄層化した際の初期 I R 不良率を改善する効果をも有する。この不良率改善の観点からは、Sc、Y、Ce、Dy、Ho、Er、Tm、Yb および Lu の少なくとも一つの酸化物を含有させることがより好ましい。第 4 副成分を添加する場合において、前記主成分 100 モルに対する前記第 4 副成分の比率は、酸化物中の R 換算で、 $0.02 \text{ モル} \leq \text{第 4 副成分} < 2 \text{ モル}$ 、好ましくは  $0.02 \text{ モル} \leq \text{第 4 副成分} \leq 0.6 \text{ モル}$  である。

【0038】なお、図 1 に示す誘電体層 2 の積層数や厚み等の諸条件は、目的や用途に応じ適宜決定すればよい。また、誘電体層 2 は、グレインと粒界相とで構成され、誘電体層 2 のグレインの平均粒子径は、 $1 \sim 5 \mu\text{m}$  程度あることが好ましい。この粒界相は、通常、誘電体材料あるいは内部電極材料を構成する材質の酸化物や、別途添加された材質の酸化物、さらには工程中に不純物として混入する材質の酸化物を成分とし、通常ガラスないしガラス質で構成されている。

#### 【0039】内部電極層 3

内部電極層 3 に含有される導電材は、特に限定されないが、誘電体層 2 の構成材料が耐還元性を有するため、卑金属を用いることができる。導電材として用いる卑金属としては、Ni または Ni 合金が好ましい。Ni 合金としては、Mn、Cr、Co および Al から選択される 1 種以上の元素と Ni との合金が好ましく、合金中の Ni 含有量は 95 重量%以上であることが好ましい。なお、Ni または Ni 合金中には、P、Fe、Mg 等の各種微量成分が 0.1 重量%程度以下含まれていてもよい。内部電極層の厚さは用途等に応じて適宜決定すればよいが、通常、 $0.5 \sim 5 \mu\text{m}$ 、特に  $1 \sim 2.5 \mu\text{m}$  程度であることが好ましい。

#### 【0040】外部電極 4

外部電極 4 に含有される導電材は、特に限定されないが、通常、Cu や Cu 合金あるいは Ni や Ni 合金等を用いる。なお、Ag や Ag-Pd 合金等も、もちろん使用可能である。なお、本実施形態では、安価な Ni、Cu や、これらの合金を用いる。外部電極の厚さは用途等に応じて適宜決定されればよいが、通常、 $10 \sim 50 \mu\text{m}$  程度であることが好ましい。

#### 【0041】積層セラミックコンデンサの製造方法

本発明の誘電体磁器組成物を用いた積層セラミックコンデンサは、従来の積層セラミックコンデンサと同様に、

ペーストを用いた通常の印刷法やシート法によりグリーンチップを作製し、これを焼成した後、外部電極を印刷または転写して焼成することにより製造される。以下、製造方法について具体的に説明する。

【0042】まず、誘電体層用ペースト、内部電極用ペースト、外部電極用ペーストをそれぞれ製造する。

#### 【0043】誘電体層用ペースト

誘電体層用ペーストは、誘電体原料と有機ビヒクルとを混練した有機系の塗料であってもよく、水系の塗料であってもよい。

【0044】誘電体原料には、前述した本発明に係る誘電体磁器組成物の組成に応じ、主成分を構成する原料と、第 1 ～ 第 4 副成分を構成する原料とが用いられる。主成分を構成する原料としては、Sr、Ca、Ti、Zr の酸化物および／または焼成により酸化物になる化合物が用いられる。第 1 副成分を構成する原料としては、V、Nb、W、Ta および Mo の酸化物および／または焼成後にこれらの酸化物になる化合物から選ばれる 1 種類以上の単一酸化物または複合酸化物が用いられる。第 2 副成分を構成する原料としては、Mn の酸化物および／または焼成により Mn の酸化物になる化合物の単一酸化物または複合酸化物が用いられる。第 3 副成分を構成する原料としては、 $\text{SiO}_2$ 、MO（ただし、M は、Ba、Ca、Sr および Mg から選ばれる少なくとも 1 種の元素）、 $\text{Li}_2\text{O}$  および  $\text{B}_2\text{O}_3$  から選ばれる少なくとも 1 種の化合物が用いられる。第 4 副成分を構成する原料としては、R の酸化物（ただし、R は、Sc、Y、La、Ce、Pr、Nd、Pm、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm、Yb および Lu から選択される少なくとも 1 種）が用いられる。

【0045】なお、焼成により酸化物になる化合物としては、例えば炭酸塩、硝酸塩、シュウ酸塩、有機金属化合物等が例示される。もちろん、酸化物と、焼成により酸化物になる化合物とを併用してもよい。誘電体原料中の各化合物の含有量は、焼成後に上記した誘電体磁器組成物の組成となるように決定すればよい。これらの原料粉末は、通常、平均粒子径  $0.0005 \sim 5 \mu\text{m}$  程度のものが用いられる。

【0046】有機ビヒクルとは、バインダを有機溶剤中に溶解したものであり、有機ビヒクルに用いられるバインダは、特に限定されず、エチルセルロース、ポリビニルブチラル等通常の各種バインダから適宜選択すればよい。また、このとき用いられる有機溶剤も特に限定されず、印刷法やシート法等利用する方法に応じてテルピネオール、ブチルカルビトール、アセトン、トルエン等の有機溶剤から適宜選択すればよい。

【0047】また、水溶性塗料とは、水に水溶性バインダ、分散剤等を溶解させたものであり、水溶性バインダは、特に限定されず、ポリビニルアルコール、セルロース、水溶性アクリル樹脂、エマルジョン等から適宜選択



すればよい。

【0048】内部電極用ペースト、外部電極用ペースト  
内部電極用ペーストは、上述した各種導電性金属や合金からなる導電材料あるいは焼成後に上述した導電材料となる各種酸化物、有機金属化合物、レジネート等と、上述した有機ビヒクルとを混練して調製される。また、外部電極用ペーストも、この内部電極用ペーストと同様にして調製される。

【0049】上述した各ペーストの有機ビヒクルの含有量は、特に限定されず、通常の含有量、たとえば、バインダは1～5重量%程度、溶剤は10～50重量%程度とすればよい。また、各ペースト中には必要に応じて各種分散剤、可塑剤、誘電体、絶縁体等から選択される添加物が含有されても良い。

【0050】印刷法を用いる場合は、誘電体ペーストおよび内部電極用ペーストをポリエチレンテレフタレート等の基板上に積層印刷し、所定形状に切断したのち基板から剥離することでグリーンチップとする。これに対して、シート法を用いる場合は、誘電体ペーストを用いてグリーンシートを形成し、この上に内部電極ペーストを印刷したのちこれらを積層してグリーンチップとする。

【0051】次に、このグリーンチップを脱バインダ処理および焼成する。

#### 【0052】脱バインダ処理

脱バインダ処理は、通常の条件で行えばよいが、特に内部電極層の導電材としてNiやNi合金等の卑金属を用いる場合には、空気雰囲気において、昇温速度を5～300℃/時間、より好ましくは10～100℃/時間、保持温度を180～400℃、より好ましくは200～300℃、温度保持時間を0.5～24時間、より好ましくは5～20時間とする。

#### 【0053】焼成

グリーンチップの焼成雰囲気は、内部電極層用ペースト中の導電材の種類に応じて適宜決定すればよいが、導電材としてNiやNi合金等の卑金属を用いる場合には、焼成雰囲気の酸素分圧を好ましくは $10^{-10}$ ～ $10^{-3}$  Paとし、より好ましくは $10^{-10}$ ～ $6 \times 10^{-5}$  Paとする。焼成時の酸素分圧が低すぎると内部電極の導電材が異常焼結を起こして途切れてしまい、酸素分圧が高すぎると内部電極が酸化されるおそれがある。特に酸素分圧を $10^{-10}$ ～ $6 \times 10^{-5}$  Paに調整することにより、優れた容量温度特性を有し、しかも絶縁抵抗の加速寿命が向上され、得られる積層型セラミックコンデンサ1の信頼性を高めることができる。

【0054】焼成の保持温度は、1000～1400℃、より好ましくは1200～1380℃である。保持温度が低すぎると緻密化が不十分となり、保持温度が高すぎると内部電極の異常焼結による電極の途切れまたは内部電極材質の拡散により容量温度特性が悪化するからである。

【0055】これ以外の焼成条件としては、昇温速度を50～500℃/時間、より好ましくは200～300℃/時間、温度保持時間を0.5～8時間、より好ましくは1～3時間、冷却速度を50～500℃/時間、より好ましくは200～300℃/時間とし、焼成雰囲気は還元性雰囲気とすることが望ましく、雰囲気ガスとしてはたとえば、窒素ガスと水素ガスとの混合ガスを加湿して用いることが望ましい。

【0056】還元性雰囲気で焼成した場合は、コンデンサチップの焼結体にアニール（熱処理）を施すことが望ましい。

#### 【0057】アニール（熱処理）

アニールは誘電体層を再酸化するための処理であり、これにより絶縁抵抗を増加させることができる。アニール雰囲気の酸素分圧は、好ましくは $10^{-4}$  Pa以上、より好ましくは $10^{-1}$ ～10 Paである。酸素分圧が低すぎると誘電体層2の再酸化が困難となり、酸素分圧が高すぎると内部電極層3が酸化されるおそれがある。特に、本発明の誘電体磁器組成物を焼成して得られる焼結体を熱処理するに際し、酸素分圧を $10^{-1}$ ～10 Paの範囲に調整することにより、初期絶縁抵抗（IR）の不良発生率改善に一層効果的である。

【0058】アニールの際の保持温度は、1100℃以下、より好ましくは500～1100℃である。保持温度が低すぎると誘電体層の再酸化が不十分となって絶縁抵抗が悪化し、その加速寿命も短くなる傾向がある。また、保持温度が高すぎると内部電極が酸化されて容量が低下するだけでなく、誘電体素地と反応してしまい、容量温度特性、絶縁抵抗およびその加速寿命が悪化する傾向がある。なお、アニールは昇温行程および降温行程のみから構成することもできる。この場合には、温度保持時間はゼロであり、保持温度は最高温度と同義である。

【0059】これ以外のアニール条件としては、温度保持時間を0～20時間、より好ましくは6～10時間、冷却速度を50～500℃/時間、より好ましくは100～300℃/時間とし、アニールの雰囲気ガスとしては、たとえば、窒素ガスを加湿して用いることが望ましい。

【0060】なお、上述した焼成と同様に、前記脱バインダ処理およびアニール工程において、窒素ガスや混合ガスを加湿するためには、たとえばウェッター等を用いることができ、この場合の水温は5～75℃とすることが望ましい。

【0061】また、これら脱バインダ処理、焼成およびアニールは連続して行っても互いに独立して行っても良い。これらを連続して行う場合には、脱バインダ処理ののち冷却することなく雰囲気を変更し、続いて焼成の際の保持温度まで昇温して焼成を行い、続いて冷却してアニールの保持温度に達したら雰囲気を変更してアニール処理を行うことがより好ましい。一方、これらを独立し



て行う場合には、焼成に関しては脱バインダ処理時の保持温度まで窒素ガスあるいは加湿した窒素ガス雰囲気下で昇温したのち、雰囲気を変更してさらに昇温を続けることが好ましく、アニールの保持温度まで冷却したのち、再び窒素ガスまたは加湿した窒素ガス雰囲気に変更して冷却を続けることが好ましい。また、アニールに関しては窒素ガス雰囲気下で保持温度まで昇温したのち雰囲気を変更しても良く、アニールの全工程を加湿した窒素ガス雰囲気としても良い。

【0062】以上のようにして得られたコンデンサ焼成体に、たとえば、バレル研磨やサンドブラストにより端面研磨を施し、外部電極用ペーストを印刷または転写して焼成し、外部電極4を形成する。外部電極用ペーストの焼成条件は、たとえば、加湿した窒素ガスと水素ガスとの混合ガス中で600～800℃にて10分～1時間程度とすることが好ましい。そして、必要に応じて外部電極4の表面にメッキ等により被覆層（パッド層）を形成する。

【0063】このようにして製造された本実施形態のセラミックコンデンサ1は、はんだ付け等によってプリント基板上に実装され、各種電子機器に用いられる。

【0064】以上本発明の実施形態について説明してきたが、本発明はこうした実施形態に何等限定されるものではなく、本発明の要旨を逸脱しない範囲内において種々なる態様で実施し得ることは勿論である。

【0065】たとえば、上述した実施形態では、本発明に係る電子部品として積層セラミックコンデンサを例示したが、本発明に係る電子部品としては、積層セラミックコンデンサに限定されず、上記組成の誘電体磁器組成物で構成してある誘電体層を有するものであれば何でも良い。

#### 【0066】

【実施例】次に、本発明の実施の形態をより具体化した実施例を挙げ、本発明をさらに詳細に説明する。但し、本発明は、これらの実施例のみに限定されるものではない。

#### 【0067】実施例1

まず、誘電体材料を作製するための出発原料として、それぞれ平均粒径0.1～1μmの主成分原料（SrCO<sub>3</sub>、CaCO<sub>3</sub>、TiO<sub>2</sub>、ZrO<sub>2</sub>）および第1～第4副成分原料を用意した。MnOの原料には炭酸塩（第2副成分：MnCO<sub>3</sub>）を用い、他の原料には酸化物（第1副成分：V<sub>2</sub>O<sub>5</sub>、第3副成分：SiO<sub>2</sub>+CaO、第4副成分：Y<sub>2</sub>O<sub>3</sub>）を用いた。なお、第3副成分であるSiO<sub>2</sub>+CaOは、SiO<sub>2</sub>およびCaOをボールミルにより16時間湿式混合し、乾燥後、1150℃で空気中で焼成し、さらに、ボールミルにより100時間湿式粉碎して得られるCaSiO<sub>3</sub>を用いても同様の特性が得られた。

【0068】これらの原料を、組成式{（Sr<sub>1-x</sub>

Ca<sub>x</sub>）O}・（Ti<sub>1-y</sub>Zr<sub>y</sub>）O<sub>2</sub>（主成分）+V<sub>2</sub>O<sub>5</sub>（第1副成分）+MnCO<sub>3</sub>（第2副成分）+（SiO<sub>2</sub>+CaO）（第3副成分）+Y<sub>2</sub>O<sub>3</sub>（第4副成分）において、焼成後の組成が表1～表3の試料1～17に示す配合比になるように秤量した後、これらをそれぞれボールミルにより、約16時間湿式混合し、これを乾燥することによって誘電体磁器組成物（誘電体材料）を得た。

【0069】このようにして得られた乾燥後の誘電体原料100重量部と、アクリル樹脂4.8重量部と、塩化メチレン40重量部と、酢酸エチル20重量部と、ミネラルスピリット6重量部と、アセトン4重量部とをボールミルで混合してペースト化し、誘電体層用ペーストを得た。

【0070】次いで、平均粒径0.2～0.8μmのNi粒子100重量部と、有機ビヒクル（エチルセルロース8重量部をブチルカルビトール92重量部に溶解したもの）40重量部と、ブチルカルビトール10重量部とを3本ロールにより混練してペースト化し、内部電極層用ペーストを得た。

【0071】次いで、平均粒径0.5μmのCu粒子100重量部と、有機ビヒクル（エチルセルロース樹脂8重量部をブチルカルビトール92重量部に溶解したもの）35重量部およびブチルカルビトール7重量部とを混練してペースト化し、外部電極用ペーストを得た。

【0072】次いで、上記誘電体層用ペーストを用いてPETフィルム上に、厚さ6μmのグリーンシートを形成し、この上に内部電極層用ペーストを印刷したのち、PETフィルムからグリーンシートを剥離した。次いで、これらのグリーンシートと保護用グリーンシート（内部電極層用ペーストを印刷しないもの）とを積層、圧着してグリーンチップを得た。内部電極を有するシートの積層数は4層とした。

【0073】次いで、グリーンチップを所定サイズに切断し、脱バインダ処理、焼成およびアニール（熱処理）を行って、積層セラミック焼成体を得た。脱バインダ処理は、昇温時間15℃/時間、保持温度280℃、保持時間8時間、空気雰囲気下の条件で行った。また、焼成は、昇温速度200℃/時間、保持温度1200～1380℃、保持時間2時間、冷却速度300℃/時間、加湿したN<sub>2</sub>+H<sub>2</sub>混合ガス雰囲気（酸素分圧は2×10<sup>-7</sup>～5×10<sup>-4</sup>Pa内に調節）の条件で行った。アニールは、保持温度900℃、温度保持時間9時間、冷却速度300℃/時間、加湿したN<sub>2</sub>ガス雰囲気（酸素分圧は3.54×10<sup>-2</sup>Pa）の条件で行った。なお、焼成およびアニールの際の雰囲気ガスの加湿には、水温を35℃としたウェッターを用いた。

【0074】次いで、積層セラミック焼成体の端面をサンドブラストにて研磨したのち、外部電極用ペーストを端面に転写し、加湿したN<sub>2</sub>+H<sub>2</sub>雰囲気中において

て、800℃にて10分間焼成して外部電極を形成し、図1に示す構成の積層セラミックコンデンサのサンプルを得た。

【0075】このようにして得られた各サンプルのサイズは、3.2mm×1.6mm×0.6mmであり、内部電極層に挟まれた誘電体層の数は4、その厚さは4μmであり、内部電極層の厚さは2μmであった。各サンプルについて下記特性の評価を行った。

【0076】比誘電率(ε<sub>r</sub>)、絶縁抵抗(IR)  
コンデンサのサンプルに対し、基準温度25℃でデジタルLCRメータ(YHP社製4274A)にて、周波数1kHz、入力信号レベル(測定電圧)1Vrmsの条件下で、静電容量を測定した。そして、得られた静電容量と、コンデンササンプルの電極寸法および電極間距離とから、比誘電率(単位なし)を算出した。その後、絶縁抵抗計(アドバンテスト社製R8340A)を用いて、25℃においてDC50Vを、コンデンササンプルに60秒間印加した後の絶縁抵抗IRを測定し、この測\*

$$\Delta C_{85}/C_{20} = \{ (C_{85} - C_{20}) / C_{20} \} \times (1/65) \quad \cdots \text{式1}$$

ただし、式1中、C<sub>85</sub>は85℃における静電容量、C<sub>20</sub>※(いずれもm=0.985)におけるV<sub>2</sub>O<sub>5</sub>の添加量(V換算)と高温負荷寿命時間との関係を図3に示した。同図から分かるように、Vの添加量が増加して

【0078】また、本実施例の代表的な試料4につき、-50℃～+150℃の温度範囲における容量変化率ΔC/Cを測定して、図2にグラフ化した。同図には20℃における容量を基準とした変化率を表している。同図からも明らかなように、良好な容量温度特性を示すことが理解できる。

【0079】高温負荷寿命(絶縁抵抗の加速寿命)  
コンデンサのサンプルに対し、175℃で8V/μmの直流電圧の印加状態に保持することにより、高温負荷寿命を測定した。この高温負荷寿命は、10個のコンデンササンプル(誘電体層の厚み4μm)について行い、平均寿命時間を測定することにより評価した。結果を表1～表3に示す。評価として、高温負荷寿命は、誘電体層を薄層化する際に特に重要となるものであり、印加開始から抵抗が一桁落ちるまでの時間を寿命と定義した。

【0080】また、本発明の実施例である試料3、4 ※

表1

試料 番号		第1副成分		焼成 温度 (℃)	比誘電率 ε	比抵抗 ρ (Ω cm)	容量温度特性	高温負荷 寿命 (時間)
		種類	モル				ΔC <sub>85</sub> /C <sub>20</sub> (ppm/℃)	
1	比較例	V	0	1300	235	1E+14	-738	0.08
2	実施例	V	0.01	1300	230	1.02E+14	-710	0.2
3	実施例	V	0.1	1300	247	1.13E+14	-720	4.2
4	実施例	V	0.2	1220	240	2.84E+13	-731	184
5	実施例	V	1.8	1220	225	3E+12	-780	763
6	比較例	V	2	1220	—	—	—	—

ただし、主成分のm=0.985

主成分のx=0.36、y=0

第2副成分(MnO<sub>2</sub>)のMn換算のモル数=0.37モル

第3副成分(SiO<sub>2</sub>+CaO)のモル数=(0.4+0.4)モル

第4副成分(Y<sub>2</sub>O<sub>3</sub>)のY換算のモル数=0.07モル

「※」=半導体化

\* 定値と、コンデンササンプルの電極面積および厚みとから、比抵抗ρ(単位はΩcm)を計算で求めた。結果を表1～表3に示す。評価として、比誘電率ε<sub>r</sub>は、小型で高誘電率のコンデンサを作成するために重要な特性であり、180以上、より好ましくは200以上を良好とした。比抵抗値は1×10<sup>12</sup>Ωcm以上を良好とした。比誘電率ε<sub>r</sub>の値は、コンデンサの試料数n=10個を用いて測定した値の平均値から求めた。比抵抗ρの値は、良品10個の比抵抗の平均値とした。

#### 【0077】静電容量の温度特性

コンデンサのサンプルに対し、LCRメータを用いて、1kHz、1Vの電圧での静電容量を測定し、基準温度を20℃としたとき、20～85℃の温度範囲内で、温度に対する静電容量変化率が-2000～0ppm/℃を満足するかどうかを調べ、結果を表1～表3に示す。容量変化率ΔC<sub>85</sub>/C<sub>20</sub>(ppm/℃)は、下記式1により算出した。

0.2モルになるときに、寿命時間は平均184時間であり、添加量が少ないときよりもコンデンサの信頼性が高いことが分かる。また、添加量0モルに比べて、2000倍以上に寿命が改善されることが確認できた。さらに、本発明の実施例である試料9～11(いずれもm=1.02)におけるV<sub>2</sub>O<sub>5</sub>の添加量(V換算)と高温負荷寿命時間との関係を図4に示した。同図から分かるように、Vの添加量が増加して0.2モルになるときに、寿命時間は平均23時間前後であり、添加量が少ないときよりもコンデンサの信頼性が高いことが分かる。また、添加量0モルに比べて、2000倍以上に寿命が改善されることが確認できた。

【0081】

【表1】

【0082】

\* \* 【表2】

表2

試料 番号		第1副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega\text{cm}$ )	容量温度特性	高温負荷 寿命 (時間)
		種類	モル				$\Delta C_{ss}/C_{ss}$ (ppm/°C)	
7	比較例	V	0	1380	215	$2E+13$	-832	<0.01
8	実施例	V	0.01	1380	223	$2.5E+13$	-853	0.1
9	実施例	V	0.05	1380	220	$4E+13$	-850	0.35
10	実施例	V	0.1	1380	230	$1E+14$	-880	2.3
11	実施例	V	0.2	1380	210	$5E+13$	-880	23
12	実施例	V	1.8	1380	212	$2E+12$	-908	78
13	比較例	V	2	1380	—*	—*	—*	—*

ただし、主成分の $m=1.02$ 主成分の $x=0.36$ 、 $y=0$ 第2副成分( $\text{MnCO}_3$ )のMn換算のモル数=0.37モル第3副成分( $\text{SiO}_2+\text{CaO}$ )のモル数=(2.5+2.5)モル第4副成分( $\text{Y}_2\text{O}_3$ )のY換算のモル数=0モル

[\*]=半導体化

【0083】

※ ※ 【表3】

表3

試料 番号		主成分 m	焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega\text{cm}$ )	容量温度特性	高温負荷 寿命 (時間)
						$\Delta C_{ss}/C_{ss}$ (ppm/°C)	
14	比較例	0.94	1220	—*	—*	—*	—*
15	実施例	0.985	1200	214	$1E+14$	-534	129
16	実施例	1.02	1380	226	$2E+14$	-842	2.2
17	比較例	1.08	1380	—**	—**	—**	—**

ただし、主成分の $x=0.36$ 、 $y=0$ 第1副成分( $\text{V}_2\text{O}_5$ )のV換算のモル数=0.1モル第2副成分( $\text{MnCO}_3$ )のMn換算のモル数=0.37モル第3副成分( $\text{SiO}_2+\text{CaO}$ )のモル数=(2.5+2.5)モル第4副成分( $\text{Y}_2\text{O}_3$ )のY換算のモル数=0.07モル

[\*]=半導体化、\*\*]=緻密化不可

【0084】表1～表3中における第1～第4副成分のモル数は、主成分100モルに対する比率である。また表1～表3中、比抵抗( $\rho$ )の数値において、「 $mE+n$ 」は「 $m \times 10^{+n}$ 」を意味する。

【0085】表1～表2に示される結果から、第1副成分の添加量につき、以下のことが理解される。試料1および試料7のようにVをまったく添加しないと、高温負荷寿命時間が極端に短い。また、試料6および試料13のようにVの添加量が2モルであると、誘電体が半導体化され、絶縁抵抗が不十分である。これに対し、第1副成分を所定量含有する試料2～5、8～12のサンプルでは、十分な比誘電率と絶縁抵抗とを有し、還元雰囲気での焼成においても還元されず、また内部電極材料であるニッケルも酸化せず、耐還元性に優れた誘電体磁器組成物が得られていることが確認でき、かつ容量温度特性が優れており、しかも高温負荷寿命(絶縁抵抗の加速寿命)を向上できることが確認できた。 $\text{V}_2\text{O}_5$ に代えて $\text{MoO}_3$ 、 $\text{WO}_3$ 、 $\text{Ta}_2\text{O}_5$ および $\text{Nb}_2\text{O}_5$ をそれぞれ添加し、上記と同様の条件でそれぞれ評価したが、何れもほぼ同じ結果が得られた。なお、試料2～5および試料8～12は本発明の実施例を

示しており、試料1、6、7、13は本発明の比較例を示している。

【0086】表3に示される結果から、主成分の $m$ の比につき、以下のことが理解される。試料14のように $m=0.94$ の場合は、還元雰囲気下における焼成で誘電体が還元され、十分な絶縁抵抗がとれず、コンデンサとして作用しないことが確認できた。また試料17のように $m=1.08$ であると、第1副成分を所定量含有させても、1380°C(高温)で焼成しても、緻密な焼結体が得られない。なお、試料15、16は本発明の実施例を示しており、試料14、17は本発明の比較例を示している。

## 【0087】実施例2

主成分の $m=1.02$ 、 $x=0.36$ 、 $y=0$ 、第1副成分(V)のモル数=0.1モル、第3副成分( $\text{SiO}_2+\text{CaO}$ )のモル数=(2.5+2.5)モル、第4副成分の(Y)のモル数=0.07モルとした以外には、第2副成分としての $\text{MnCO}_3$ の添加量(Mn換算)を、表4に示すように変化させて評価した。結果を表4に示す。

【0088】

【表4】

表4

試料 番号		第2副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega\text{cm}$ )	容量温度特性 $\Delta C_{15}/C_{20}$ (ppm/°C)	高温負荷 寿命 (時間)	初期IR 不良率 (%)
		種類	モル						
18	実施例	Mn	0	1380	218	$8.5\text{E}+12$	-810	0.02	80
19	実施例	Mn	0.05	1380	217	$9.82\text{E}+12$	-825	0.1	82
20	実施例	Mn	0.37	1380	220	$2\text{E}+14$	-841	2.2	23
21	実施例	Mn	0.73	1380	221	$8.88\text{E}+13$	-1238	13	10
22	実施例	Mn	1.5	1380	210	$2\text{E}+13$	-1678	20	7
23	実施例	Mn	3.8	1380	205	$1.3\text{E}+12$	-1846	32	8
24	比較例	Mn	4	1380	198	$<1\text{E}+12$	-1984	x	x

ただし、主成分の $m=1.02$ 主成分の $x=0.36, y=0$ 第1副成分( $\text{V}_2\text{O}_5$ )のV換算のモル数=0.1モル第3副成分( $\text{SiO}_2+\text{CaO}$ )のモル数=(2.5+2.5)モル第4副成分( $\text{Y}_2\text{O}_3$ )のY換算のモル数=0.07モル

【0089】表4に示されるように、第2副成分(Mn換算)の添加量が4モルであると、初期絶縁抵抗が低下し、第2副成分の添加量が0モル $\leq$ 第2副成分 $<$ 4モルの範囲では、添加量が多い(3.8モル)ほど、高温負荷寿命(絶縁抵抗の加速寿命)が向上され、しかも初期IR不良率の発生も低減でき、添加量が少ない(0モル)ほど、容量温度変化率が小さくなることが確認できた。

【0090】なお、初期IR不良率の値は、100個程度のコンデンササンプルの比抵抗 $\rho$ を、絶縁抵抗IRと、電極面積および誘電体層の厚み(本実施例では4 $\mu\text{m}$ )とから、計算でそれぞれ求め、バルクの状態のときの比抵抗 $\rho$ の値より一桁以上小さい試料の個数を、全体個数で割って、パーセンテージで示した。この値が小さいほど、初期IR不良率が低く、良品が多いこととなる。

【0091】また、試料19, 20につき、 $-50^\circ\text{C} \sim 30$   
+150 $^\circ\text{C}$ の温度範囲における容量変化率 $\Delta C/C$ を測\*

\*定して、図5にグラフ化した。同図には20 $^\circ\text{C}$ における容量を基準とした変化率を表している。同図から分かるように、試料19, 20の何れも良好な容量温度特性を示すことが確認できる。

【0092】なお、 $\text{MnCO}_3$ に代えて $\text{MnO}$ を添加し、上記と同様の条件でそれぞれ評価したが、何れも同じ結果が得られた。

#### 実施例3

主成分の $m=0.985, x=0.36, y=0$ 、第1副成分(V換算)のモル数=0.2モル、第2副成分(Mn換算)のモル数=0.37モル、第4副成分の(Y換算)のモル数=0.07モルとした以外には、第3副成分としての( $\text{SiO}_2 + \text{CaO}$ )の添加量を、表5に示すように変化させて、高温負荷寿命の改善の程度を試験した。結果を表5に示す。

【0093】

【表5】

試料 番号		第3副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega\text{cm}$ )	容量温度特性 $\Delta C_{15}/C_{20}$ (ppm/°C)	高温負荷 寿命 (時間)	初期IR 不良率 (%)
		種類	モル						
4-1	比較例	$\text{SiO}_2+\text{CaO}$	0	1380	—**	—**	—**	—**	—**
4	実施例	$\text{SiO}_2+\text{CaO}$	0.4+0.4	1220	340	$2.84\text{E}+13$	-731	184	84
4-2	実施例	$\text{SiO}_2+\text{CaO}$	2.5+2.5	1220	219	$3.78\text{E}+13$	-833	220	72
4-3	実施例	$\text{SiO}_2+\text{CaO}$	4+4	1220	222	$3.5\text{E}+13$	-873	223	76
4-4	実施例	$\text{SiO}_2+\text{CaO}$	5+5	1220	183	$2.5\text{E}+13$	-908	168	73
4-5	実施例	$\text{SiO}_2+\text{CaO}$	6.9+6.9	1220	182	$8\text{E}+12$	-987	125	88
4-6	比較例	$\text{SiO}_2+\text{CaO}$	7.5+7.5	1220	175	$2\text{E}+12$	-1038	88	85

ただし、主成分の $m=0.985$ 主成分の $x=0.36, y=0$ 第1副成分( $\text{V}_2\text{O}_5$ )のV換算のモル数=0.2モル第2副成分( $\text{MnCO}_3$ )のMn換算のモル数=0.37モル第4副成分( $\text{Y}_2\text{O}_3$ )のY換算のモル数=0.07モル

「\*\*」=測定不能

【0094】表5に示されるように、第3副成分の添加量を0モルより多くすることにより、焼結性が改善された。添加量を15モル未満とすることにより、比誘電率の低下を抑え、十分な容量を確保できることも確認できた。なお、初期IR不良率の値は、実施例2と同様にして求めた。なお、( $\text{SiO}_2 + \text{CaO}$ )の代わりに $\text{CaSiO}_3$ を用いても同様の結果が得られた。

#### 【0095】実施例4

誘電体層の厚みを図6に示すように異ならせた以外は、表4に示される実施例2の試料20と同様にしてコンデンササンプルを複数個作製した(試料25)。また、第3副成分として $\text{SiO}_2$ を用い、誘電体層の厚みを図6に示すように異ならせた以外は、表4に示される実施例2の試料20と同様にしてコンデンササンプルを複数

個作製した(試料26)。これらのコンデンササンプルを用いて、第3副成分の種類が誘電体層を薄層化したときの初期絶縁抵抗(IR)に与える影響を確認する試験を行った。結果を図6に示すが、同図からも分かるように、第3副成分として( $\text{SiO}_2 + \text{CaO}$ )を用いた方が、誘電体層の薄層化に対しても初期絶縁抵抗(IR)のバラツキが少ないことが確認できた。なお、( $\text{SiO}_2 + \text{CaO}$ )の代わりに $\text{CaSiO}_3$ を用いても同様の結果が得られた。

#### 【0096】実施例5

誘電体層の厚みを $7\mu\text{m}$ 以上、 $4\mu\text{m}$ 、 $2\mu\text{m}$ と異ならせた以外は、表4に示される実施例2の試料20と同様にしてコンデンササンプルを複数個作製し(試料27~29)、また第3副成分としての( $\text{SiO}_2 + \text{CaO}$ )にさらに $\text{Li}_2\text{O}$ を1.4モル添加し、誘電体層の厚みを $7\mu\text{m}$ 以上、 $4\mu\text{m}$ 、 $2\mu\text{m}$ と異ならせた以外は、表4に示される実施例2の試料20と同様にしてコンデンササンプルを複数個作製し(試料30~32)、これらサンプルの初期絶縁抵抗(IR)の不良発生率を算出した。結果を図7(A)~図7(C)に示すが、 $\text{Li}_2\text{O}$ を添加しても、厚みが $7\mu\text{m}$ 以上と厚いときには、不良発生率には影響を与えないが(図7(A)参照)、 $4\mu\text{m}$ 、 $2\mu\text{m}$ と薄くなってくるにつれて、 $\text{Li}_2\text{O}$ 添加の効果が表れることが確認できた(図7(B)~(C)参照)。なお、初期IR不良率の値は、実施例2と同様にして求めた。

#### 【0097】実施例6

第3副成分( $\text{SiO}_2 + \text{CaO}$ )の添加量を5.0モルとした以外は、表1に示される実施例1の試料3と同様にしてコンデンササンプルを作製した(試料33)。また、第4副成分としてのYを添加せず、第3副成分( $\text{SiO}_2 + \text{CaO}$ )の添加量を5.0モルとした以外は、表1に示される実施例1の試料3と同様にしてコンデンササンプルを作製した(試料34)。これらのコンデンササンプルを用いて、第4副成分としてのYの添加の有無が、高温負荷寿命(絶縁抵抗の加速寿命)に与える影響を確認するための試験を行った。結果を図8に示すが、同図からも分かるように、Yを添加した方が、高温負荷寿命を向上させることが確認できた。

#### 【0098】実施例7

熱処理工程における酸素分圧を、 $3.54 \times 10^{-2} \text{ Pa}$  ( $900^\circ\text{C}$ 、9時間、ウェッター温度 $35^\circ\text{C}$ )、 $4.23 \times 10^{-1} \text{ Pa}$  ( $1100^\circ\text{C}$ 、3時間、ウェッター温度 $35^\circ\text{C}$ )とし、誘電体層の厚みを $9\mu\text{m}$ (試料35~36)、 $4\mu\text{m}$ (試料37~38)と異ならせた以外は、表1に示される実施例1の試料4と同様にしてサンプルを複数個作製し、これらサンプルの初期絶縁抵抗(IR)の不良発生率を算出した。結果を図9(A)~図9(B)に示すが、誘電体層の厚みが $9\mu\text{m}$ と厚いときには、酸素分圧の違いは不良発生率には影響を与えな

いが(図9(A)参照)、 $4\mu\text{m}$ と薄くなると、酸素分圧を、 $10^{-4} \text{ Pa}$ 以上(ちなみに、 $10^{-1} \sim 10 \text{ Pa}$ の範囲内でもある)である $4.23 \times 10^{-1} \text{ Pa}$

(試料38)に調整した場合の効果が表れることが確認できた(図9(B)参照)。初期IR不良率の値は、実施例2と同様にして求めた。なお、熱処理工程における酸素分圧を $9.61 \times 10^{-2} \text{ Pa}$  ( $1100^\circ\text{C}$ 、3時間、ウェッター温度 $0^\circ\text{C}$ )にして、試料35~36および試料37~38と同様に初期絶縁抵抗の不良率発生

10 低減の効果を確認してみたが(試料39~40、特にそのような効果は確認されなかった。このことから、熱処理時の保持温度がサンプルの初期絶縁抵抗の不良発生率の低減に寄与しているものではなく、熱処理時の酸素分圧が寄与しているものと考えられる。

#### 【0099】実施例8

第3副成分を、( $\text{SiO}_2 + \text{CaO}$ ) = (0.4 + 0.4)モル( $p=0$ )、( $\text{SiO}_2 + \text{CaO} + \text{SrO}$ ) = (0.4 + 0.2 + 0.2)モル( $p=0.5$ )、および( $\text{SiO}_2 + \text{SrO}$ ) = (0.4 + 0.4)モル( $p=1$ )とし、かつ、アニールを、保持温度 $1100^\circ\text{C}$ 、温度保持時間3時間、加湿した $\text{N}_2$ ガス雰囲気(酸素分圧は $4.23 \times 10^{-1} \text{ Pa}$ )で行った以外は、試料4と同様にしてコンデンササンプルを複数個作製した(試料41、42、43)。そして、第3副成分としての( $\text{Sr}_p, \text{Ca}_{1-p}$ ) $\text{SiO}_3$ において、Srの含有割合が、コンデンササンプルにおける初期絶縁抵抗(IR)の良品率にどのような影響を与えるか評価した。結果を図10に示す。図10に示される結果から、Srの含有割合が多くなるほど、初期IRの良品率が75%(試料41)、83%(試料42)、100%(試料43)と向上していき、すなわち初期IRの不良率が25%、17%、0%と低下していくことが確認できた。なお、初期IRの不良率の値は、実施例2と同様にして求めた。

#### 【0100】

【発明の効果】以上説明してきたように、本発明によれば、焼成時の耐還元性に優れ、焼成後には優れた容量温度特性を有し、しかも絶縁抵抗の加速寿命を向上させることができる誘電体磁器組成物を提供することができる。また、本発明によれば、優れた容量温度特性を有し、しかも絶縁抵抗の加速寿命が向上され、信頼性が高められたチップコンデンサなどの電子部品を提供することができる。さらに本発明によれば、電子部品に求められる信頼性を維持しながら、初期絶縁抵抗の不良率の発生を改善できる電子部品の製造方法を提供することもできる。

#### 【図面の簡単な説明】

【図1】 図1は本発明の一実施形態に係る積層セラミックコンデンサの断面図である。

【図2】 図2は本発明の実施例である試料4の容量温

度特性を示すグラフである。

【図3】 図3は本発明の実施例である試料3、4におけるVの添加量と高温負荷寿命時間との関係を示すグラフである。

【図4】 図4は本発明の実施例である試料9～11におけるVの添加量と高温負荷寿命時間との関係を示すグラフである。

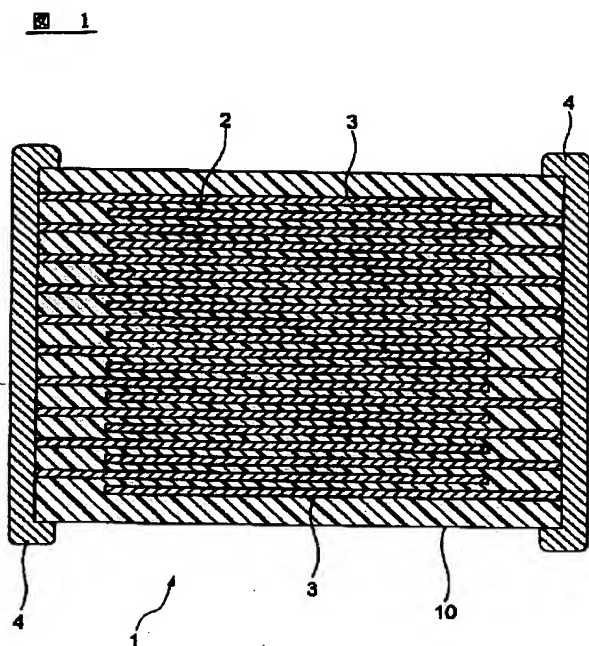
【図5】 図5は本発明の実施例である試料19、20の容量温度特性を示すグラフである。

【図6】 図6は第3副成分の種類を代えたときの、誘電体層の厚みと初期絶縁抵抗との関係を示すグラフである。

【図7】 図7は誘電体層の厚みを代えたときに、Li添加の有無と初期絶縁抵抗の不良率との関係を示すグラフである。

\*

【図1】



\* 【図8】 図8は第4副成分としてのYの添加の有無と、高温負荷寿命との関係を示すグラフである。

【図9】 図9は誘電体層の厚みを代えたときに、熱処理工程における酸素分圧と初期絶縁抵抗の不良率との関係を示すグラフである。

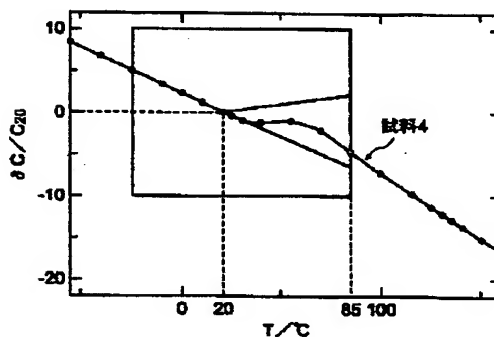
【図10】 図10は第3副成分としての（Sr，Ca）SiO<sub>3</sub>においてSrの含有割合と、コンデンササンプルの初期絶縁抵抗（IR）の良品率との関係を示すグラフである。

【符号の説明】

- 1… 積層セラミックコンデンサ
- 10… コンデンサ素子本体
- 2… 誘電体層
- 3… 内部電極層
- 4… 外部電極

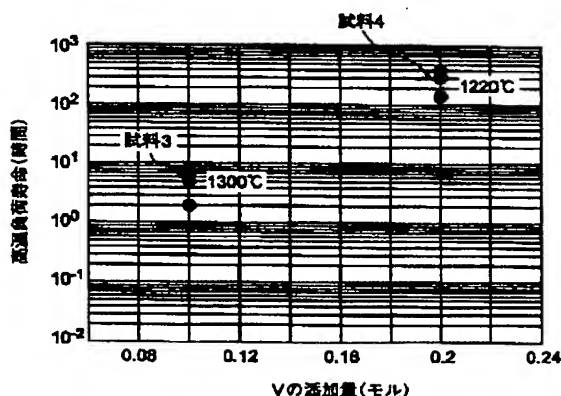
【図2】

図 2



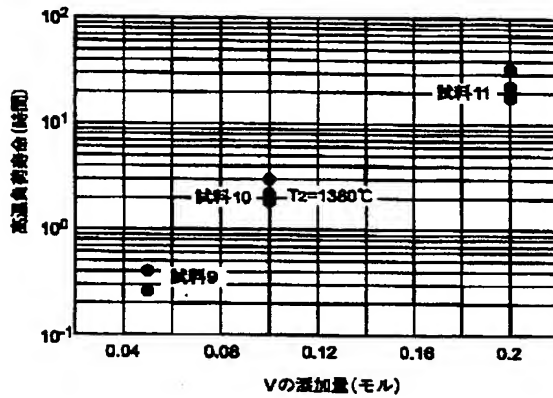
【図3】

図 3



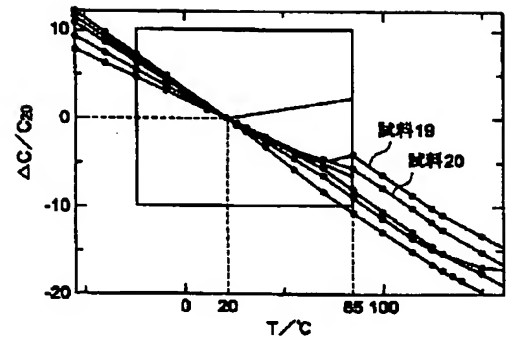
【図 4】

図 4



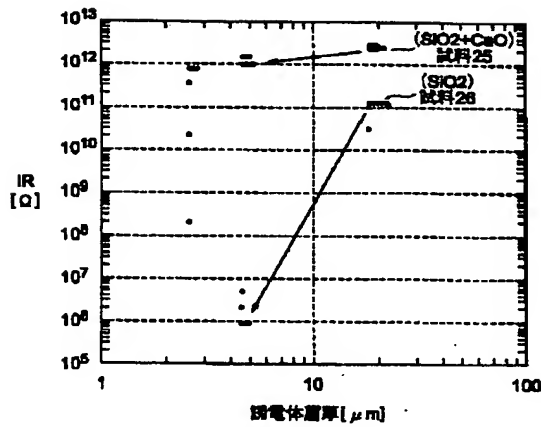
【図 5】

図 5



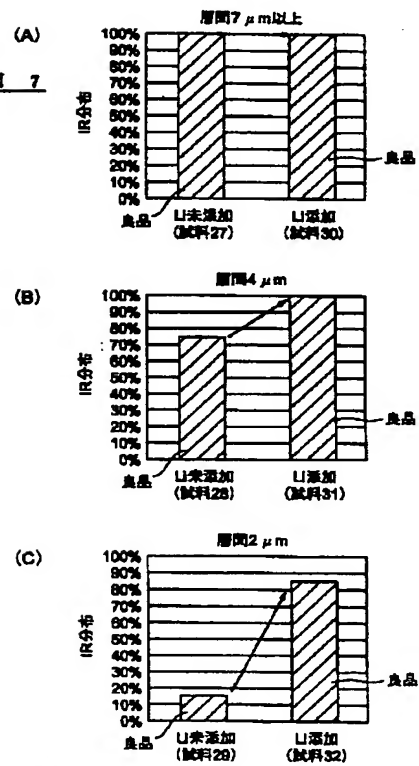
【図 6】

図 6



【図 7】

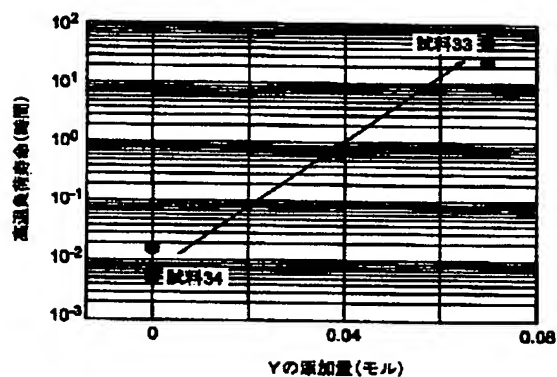
図 7





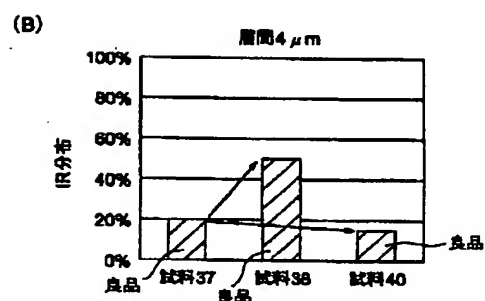
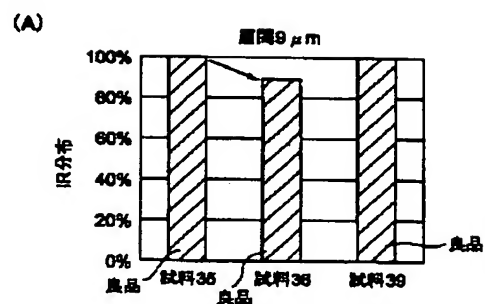
【図 8】

図 8



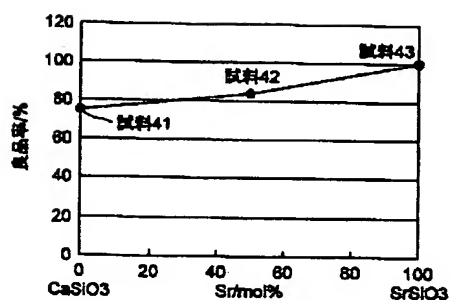
【図 9】

図 9



【図 10】

図 10



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CLAIMS

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[Claim(s)]

[Claim 1]  $\{(Sr_{1-x}Ca_x)O\}_m - (Ti_{1-y}Zr_y)O_2$  The principal component containing the dielectric oxide of the presentation shown, It is the dielectric porcelain constituent which has at least the 1st accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking. The notations  $m$  and  $y$  which show the presentation mole ratio in the formula contained in said principal component the ratio of said 1st accessory constituent [ as opposed to / have the relation of  $0.94 < m < 1.08$ ,  $0 \leq x \leq 1.00$ , and  $0 \leq y \leq 0.20$ , and / 100 mols of said principal components ] -- the metallic element conversion in an oxide --  $0.01 \text{ mol} \leq$  -- the 1st -- the dielectric porcelain constituent which is accessory constituent  $< 2 \text{ mol}$ .

[Claim 2] the ratio of said 2nd accessory constituent [ as opposed to / have further the 2nd accessory constituent containing the compound which turns into an oxide of Mn by the oxide of Mn, and/or baking, and / 100 mols of said principal components ] -- the metallic element conversion in an oxide --  $0 \text{ mol} \leq$  -- the 2nd -- the dielectric porcelain constituent according to claim 1 which is accessory constituent  $< 4 \text{ mol}$ .

[Claim 3]  $SiO_2 MO$  (however, at least one sort of elements with which M is chosen from Ba, calcium, Sr, and Mg), and  $Li_2O$  and  $B_2O_3$  from -- the ratio of said 3rd accessory constituent [ as opposed to / have further the 3rd accessory constituent containing at least one sort chosen, and / 100 mols of said principal components ] -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- dielectric porcelain constituent according to claim 1 or 2 which is accessory constituent  $< 15 \text{ mol}$ .

[Claim 4]  $(Sr_p, \text{calcium}_{1-p}) SiO_3$  (however,  $0.3 \leq p \leq 1$ ) the ratio of said 3rd accessory constituent [ as opposed to / have the 3rd included accessory constituent further and / 100 mols of said principal components ] -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- dielectric porcelain constituent according to claim 1 or 2 which is accessory constituent  $< 15 \text{ mol}$ .

[Claim 5] A dielectric porcelain constituent given in any of claims 1-4 whose electrostatic-capacity rate of change ( $\frac{\Delta C}{C}$ ) to temperature is  $-2000-0 \text{ ppm}$  (however, reference temperature of electrostatic capacity  $C$   $20 \text{ degrees C}$ )/ $\text{degree C}$  in an at least  $20-85\text{-degree C}$  temperature requirement they are.

[Claim 6] Are the electronic parts which have a dielectric layer and said dielectric layer is constituted from a dielectric porcelain constituent. Said dielectric porcelain constituent is  $\{(Sr_{1-x}Ca_x)O\}_m - (Ti_{1-y}Zr_y)O_2$  The principal component containing the dielectric oxide of the presentation shown, It has at least the 1st accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking. The notations  $m$  and  $y$  which show the presentation mole ratio in the formula contained in said principal component the ratio of said 1st accessory constituent [ as opposed to / have the relation of  $0.94 < m < 1.08$ ,  $0 \leq x \leq 1.00$ , and  $0 \leq y \leq 0.20$ , and / 100 mols of said principal components ] -- the metallic element conversion in an oxide --  $0.01 \text{ mol} \leq$  -- the 1st -- the electronic parts which are accessory constituent  $< 2 \text{ mol}$ .

[Claim 7] Electronic parts according to claim 6 which have the capacitor element body with which the laminating of the internal electrode layer has been carried out by turns with said dielectric layer.

[Claim 8] Electronic parts according to claim 7 whose electric conduction material contained in said

internal electrode layer is nickel or a nickel alloy.

[Claim 9]  $\{(Sr_{1-x}Ca_x)O\}_m-(Ti_{1-y}Zr_y)O_2$  The principal component containing the dielectric oxide of the presentation shown, It has at least the 1st accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking. The notations  $mx$  and  $y$  which show the presentation mole ratio in the formula contained in said principal component Have the relation of  $0.94 < m < 1.08$ ,  $0 \leq x \leq 1.00$ , and  $0 \leq y \leq 0.20$ , and the ratio of said 1st accessory constituent to 100 mols of said principal components by the metallic element conversion in an oxide  $0.01 \text{ mol} \leq$  -- the 1st -- with the process which produces a dielectric paste using the dielectric porcelain constituent which is accessory constituent  $< 2 \text{ mol}$  The process which produces the paste for internal electrodes, and the process which carries out the laminating of said dielectric paste and the paste for internal electrodes by turns, and obtains a layered product, The manufacture approach of electronic parts of having the baking process which calcinates said layered product and obtains a sintered compact, and the process at which oxygen tension heat-treats said sintered compact under the ambient atmosphere of  $10^{-4}$  or more Pa.

[Claim 10] said baking process -- setting -- said layered product -- oxygen tension --  $10^{-10}$  - the manufacture approach of the electronic parts according to claim 9 calcinated under the ambient atmosphere which is ten to  $3 \text{ Pa}$ .

[Claim 11] The manufacture approach of electronic parts according to claim 9 or 10 using nickel or a nickel alloy as said paste for internal electrodes.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to electronic parts using the dielectric porcelain constituent used as a dielectric layer of for example, a laminating mold ceramic condenser etc., and its dielectric porcelain constituent as a dielectric layer, and its manufacture approach.

[0002]

[Description of the Prior Art] The laminating mold ceramic condenser which is an example of electronic parts carries out the laminating of the green sheet of two or more sheets which printed conductive paste on the green sheet which consists of a predetermined dielectric porcelain constituent, and printed this conductive paste, calcinates a green sheet and an internal electrode in one, and is formed.

[0003] When the conventional dielectric porcelain constituent was calcinated under the neutrality which is a hypoxia partial pressure, or a reducing atmosphere, it was returned and it had the semi-conductor-ized property. For this reason, it was obliged to face manufacturing a laminating mold ceramic condenser and to calcinate under the oxidizing atmosphere which is a hyperoxia partial pressure. In connection with this, it did not need to fuse as a dielectric porcelain constituent and an internal electrode ingredient calcinated by coincidence at the temperature which this dielectric porcelain constituent sinters, but the expensive noble metals (for example, palladium, platinum, etc.) which do not oxidize even if it calcinates under an oxidizing quality ambient atmosphere needed to be used, and it had become big hindrance to low-pricing of the laminating mold ceramic condenser manufactured.

[0004] On the other hand, in order to use cheap base metal (for example, nickel, copper, etc.) as an ingredient of an internal electrode, it is required to develop the dielectric porcelain constituent which does not semi-conductor-ize even if it calcinates at low temperature under neutrality or a reducing atmosphere, namely, is excellent in reducibility-proof, and has specific inductive capacity sufficient after baking and outstanding dielectric characteristics (for example, the rate of a capacity temperature change is small).

[0005] Conventionally, various proposals are made as a dielectric porcelain constituent which can use base metal as an ingredient of an internal electrode.

[0006] for example, in JP,63-224108,A ( $\text{Sr}_{1-x}\text{Cax}$ )<sub>m</sub> ( $\text{Ti}_{1-y}\text{Zry}$ )<sub>03</sub> The dielectric oxide of the presentation shown Use ( $0.30 \leq x \leq 0.50$ ,  $0.03 \leq y \leq 0.20$ ,  $0.95 \leq m \leq 1.08$ ) as a principal component, and this principal component 100 weight section is received. [ however, ] As an accessory constituent, it is Mn MnO<sub>2</sub> It is the 0.01 - 2.00 weight section and SiO<sub>2</sub> by conversion. The dielectric porcelain constituent which carries out 0.10-4.00 weight section content is indicated.

[0007] Moreover, at JP,63-224109,A, it is said Mn and SiO<sub>2</sub> to said principal component. In addition, the dielectric porcelain constituent which carries out 0.01-1.00 weight section content of the ZnO further is indicated.

[0008] Furthermore, at JP,4-206109,A, it is m ( $\text{Sr}_{1-x}\text{Cax}$ ) ( $\text{Ti}_{1-y}\text{Zry}$ )<sub>03</sub>. The dielectric porcelain constituent which uses the dielectric oxide (however,  $0.30 \leq x \leq 0.50$ ,  $0.00 \leq y \leq 0.20$ ,  $0.95 \leq m \leq 1.08$ ) of the presentation shown as a principal component, and has made the powder particle size the range of

0.1-1.0 micrometers is indicated.

[0009] Further again in JP,62-24388,B (MeO) k Use as a principal component the dielectric oxide (however, the metal and k as which Me was chosen from Sr, calcium, and Sr+calcium 1.00-1.04) of the presentation shown by  $\text{TiO}_2$ , and this principal component 100 weight section is received. As a glass component, it is  $\text{Li}_2$ . The dielectric porcelain constituent which carries out 0.2-10.0 weight section content of what used O, M (however, at least one sort of metallic oxides with which M is chosen from  $\text{BaO}$ ,  $\text{CaO}$ , and  $\text{SrO}$ ), and  $\text{SiO}_2$  by the predetermined mole ratio is indicated.

[0010]

[Problem(s) to be Solved by the Invention] However, in a dielectric porcelain constituent given [ these ] in an official report, all, accelerated aging of the insulation resistance after baking was short, and when the laminating mold ceramic condenser which has internal electrodes made from base metal, such as nickel, using this dielectric porcelain constituent was manufactured, there was a problem that the dependability of the laminating mold ceramic condenser obtained became low.

[0011] The purpose of this invention has the capacity temperature characteristic which was excellent in the reducibility-proof at the time of baking, and was excellent after baking, and is to offer the dielectric porcelain constituent which can moreover raise accelerated aging of insulation resistance. Moreover, the purpose of this invention is offering electronic parts, such as a chip capacitor with which it has the outstanding capacity temperature characteristic, accelerated aging of insulation resistance moreover improved, and dependability's was raised. Furthermore, the purpose of this invention is offering the manufacture approach of electronic parts the outbreak of the percent defective of initial insulation resistance being improvable, maintaining the dependability for which electronic parts are asked.

[0012]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the dielectric porcelain constituent concerning this invention  $\{(\text{Sr}_{1-x}\text{Ca}_x)\text{O}\}_m - (\text{Ti}_{1-y}\text{Zr}_y)\text{O}_2$  The principal component containing the dielectric oxide of the presentation shown, It is the dielectric porcelain constituent which has at least the 1st accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking. The notations  $m_x$  and  $y$  which show the presentation mole ratio in the formula contained in said principal component the ratio of said 1st accessory constituent [ as opposed to / have the relation of  $0.94 < m < 1.08$ ,  $0 \leq x \leq 1.00$ , and  $0 \leq y \leq 0.20$ , and / 100 mols of said principal components ] -- the metallic element conversion in an oxide --  $0.01 \text{ mol} \leq$  -- the 1st -- it is characterized by being accessory constituent  $< 2 \text{ mol}$ .

[0013] the ratio of said 2nd accessory constituent [ as opposed to / the dielectric porcelain constituent concerning this invention has further preferably the 2nd accessory constituent containing the compound which turns into an oxide of Mn by the oxide of Mn, and/or baking, and / 100 mols of said principal components ] -- the metallic element conversion in an oxide --  $0 \text{ mol} \leq$  -- the 2nd -- it is accessory constituent  $< 4 \text{ mol}$ .

[0014] the dielectric porcelain constituent preferably applied to this invention --  $\text{SiO}_2$  MO (however, at least one sort of elements with which M is chosen from Ba, calcium, Sr, and Mg), and  $\text{Li}_2\text{O}$  and  $\text{B}_2\text{O}_3$  from -- the ratio of said 3rd accessory constituent [ as opposed to / have further the 3rd accessory constituent containing at least one sort chosen, and / 100 mols of said principal components ] -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- it is accessory constituent  $< 15 \text{ mol}$ . It is thought that the 3rd accessory constituent functions as sintering acid.

[0015] Especially the desirable mode of the 3rd accessory constituent is as being shown below. the dielectric porcelain constituent more preferably applied to this invention --  $\text{SiO}(\text{Sr}_p, \text{calcium}_{1-p})_3$  (however,  $p$   $0.3 \leq p \leq 1$ ) the ratio of said 3rd accessory constituent [ as opposed to / have the 3rd included accessory constituent further and / 100 mols of said principal components ] -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- it is accessory constituent  $< 15 \text{ mol}$ . It is thought that this kind of the 3rd accessory constituent functions as sintering acid.

[0016] Preferably, -2000-0 ppm ( $^{\circ}\text{C}$ ) / of -1500-0 ppm / of electrostatic-capacity rate of change [ as opposed to temperature in the dielectric porcelain constituent concerning this invention ] are [ degree C / degree C ] -1000-0 ppm/degree C in an at least 20-85-degree C temperature requirement. However, the

reference temperature of electrostatic capacity C is 20 degrees C.

[0017] In order to attain the above-mentioned purpose, the electronic parts concerning this invention are electronic parts which have a dielectric layer, and said dielectric layer is characterized by constituting from a dielectric porcelain constituent of one of the above.

[0018] Preferably, the electronic parts concerning this invention have the capacitor element body with which the laminating of the internal electrode layer has been carried out by turns with said dielectric layer.

[0019] Preferably, the electric conduction material by which the electronic parts concerning this invention are contained in said internal electrode layer is nickel or a nickel alloy.

[0020] In order to attain the above-mentioned purpose, the manufacture approach of the electronic parts concerning this invention The process which produces a dielectric paste using the dielectric porcelain constituent of one of the above, The process which produces the paste for internal electrodes, and the process which carries out the laminating of said dielectric paste and the paste for internal electrodes by turns, and obtains a layered product, It has the baking process which calcinates said layered product and obtains a sintered compact, and the process at which oxygen tension heat-treats preferably 10 - 4 or more Pa of said sintered compact under a 10-1-10Pa ambient atmosphere.

[0021] the manufacture approach of the electronic parts preferably built over this invention -- said baking process -- setting -- said layered product -- oxygen tension -- 10-10 - it calcinates under the ambient atmosphere which is ten to 3 Pa.

[0022] Preferably, the manufacture approach of the electronic parts concerning this invention uses nickel or a nickel alloy as said paste for internal electrodes. In addition, SiO<sub>2</sub> contained in the 3rd accessory constituent in the dielectric porcelain constituent concerning this invention MO, Li<sub>2</sub> O, B<sub>2</sub> O<sub>3</sub> And (Srp , calcium1-p ) SiO<sub>3</sub> At least, each is the meaning which should just be such a presentation after baking, and also contains the compound which turns into these oxides after baking.

[0023]

[Function] In the dielectric porcelain constituent concerning this invention, while having the capacity temperature characteristic which was excellent in the reducibility-proof at the time of baking, and was excellent after baking to the principal component containing the dielectric oxide of a specific presentation by carrying out specified quantity addition of the 1st specific accessory constituent, compared with the case where the 1st accessory constituent is not added, accelerated aging of insulation resistance improves more than 1000 times (for example, 175 degrees C, DC8v/micrometer).

[0024] Since it has the dielectric layer constituted from electronic parts, such as a chip capacitor concerning this invention, with the dielectric porcelain constituent concerning this invention, it has the outstanding capacity temperature characteristic (for example, the SL property of JIS is satisfied), moreover accelerated aging of insulation resistance improves, and the dependability of electronic parts improves.

[0025] By the manufacture approach of the electronic parts concerning this invention, the outbreak of the percent defective of initial insulation resistance is efficiently improvable, maintaining the dependability for which electronic parts, such as a chip capacitor, are asked by having the process at which oxygen tension heat-treats the sintered compact obtained by baking under the ambient atmosphere of 10 - 4 or more Pa.

[0026]

[Embodiment of the Invention] Hereafter, this invention is explained based on the operation gestalt shown in a drawing. The sectional view of the stacked type ceramic condenser which drawing 1 requires for 1 operation gestalt of this invention, The graph which shows the capacity temperature characteristic of the sample 4 whose drawing 2 is the example of this invention, the graph which shows the relation of the addition of V and elevated-temperature load lifetime in the samples 3 and 4 whose drawing 3 is the examples of this invention, The graph which shows the relation of the addition of V and elevated-temperature load lifetime in the samples 9-11 whose drawing 4 is the examples of this invention, When the thickness of a dielectric layer is replaced with, the graph and drawing 7 which show the relation between the thickness of a dielectric layer when the graph and drawing 6 which show the capacity



temperature characteristic of the samples 19 and 20 whose drawing 5 is the examples of this invention replace the class of the 3rd accessory constituent with, and initial insulation resistance When the thickness of a dielectric layer is replaced with, the graph which shows the relation between the existence of Li addition, and the percent defective of initial insulation resistance, the graph with which drawing 8 shows the existence of addition of Y as the 4th accessory constituent, and relation with an elevated-temperature load life, and drawing 9 the graph and drawing 10 which show the relation between the oxygen tension in a heat treatment process, and the percent defective of initial insulation resistance --  $\text{SiO}(\text{Sr}, \text{calcium})_3$  as the 3rd accessory constituent setting -- content of Sr -- it is the graph which shows relation with the rate of an excellent article of the initial insulation resistance (IR) of a capacitor sample comparatively.

[0027] As shown in stacked type ceramic condenser drawing 1, the stacked type ceramic condenser 1 as electronic parts concerning 1 operation gestalt of this invention has the capacitor element body 10 of a configuration of that the laminating of a dielectric layer 2 and the internal electrode layer 3 was carried out by turns. The external electrode 4 of the internal electrode layer 3 arranged by turns inside the component body 10 and the pair through which it flows respectively is formed in the both ends of this capacitor element body 10. Although there is especially no limit in the configuration of the capacitor element body 10, it usually considers as the shape of a rectangular parallelepiped. Moreover, although what is necessary is for there to be especially no limit also in the dimension, and just to consider as a suitable dimension according to an application, it is usually  $x(0.6\text{-}5.6\text{mm}) (0.3\text{-}5.0\text{mm}) \times (0.3\text{-}1.9\text{mm})$  extent. The laminating of the internal electrode layer 3 has been carried out so that each end face may be exposed to the front face of two edges where the capacitor element body 10 counters by turns. It is formed in the both ends of the capacitor element body 10, it connects with the exposure end face of the internal electrode layer 3 arranged by turns, and the external electrode 4 of a pair constitutes a capacitor circuit.

[0028] Dielectric layer 2 dielectric layer 2 contains the dielectric porcelain constituent of this invention. The dielectric porcelain constituent of this invention is  $\{(\text{Sr}_{1-x}\text{Ca}_x)\text{O}\}_m \cdot (\text{Ti}_{1-y}\text{Zr}_y)\text{O}_2$  It has the 1st accessory constituent including one or more kinds chosen from the principal component containing the dielectric oxide of the presentation shown, and the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking at least. Under the present circumstances, the amount of oxygen (O) may be deflected from the stoichiometric composition of the above-mentioned formula a little.

[0029] the inside of the above-mentioned formula, and  $x -- 0 \leq x \leq 1.00$  -- it is  $0.30 \leq x \leq 0.50$  preferably.  $x$  expresses calcium atomic number and it becomes possible to shift the phase transition point of a crystal to arbitration by changing  $x$ , i.e., a calcium/Sr ratio. Therefore, a capacity temperature coefficient and specific inductive capacity are controllable to arbitration. If  $x$  is made into the above-mentioned range, the phase transition point of a crystal can exist near a room temperature, and the temperature characteristic of electrostatic capacity can be raised. However, in this invention, the ratio of Sr and calcium is arbitrary and may contain only one side.

[0030] the inside of the above-mentioned formula, and  $y -- 0 \leq y \leq 0.20$  -- it is  $0 \leq y \leq 0.10$  preferably. Decline in specific inductive capacity is prevented by making  $y$  or less into 0.20.  $y$  is  $\text{TiO}_2$  although Zr atomic number is expressed.  $\text{ZrO}_2$  which compares and is hard to be returned There is an inclination which reducibility-proof increases further by permuting. However, in this invention, Zr does not necessarily need to be included and only Ti may be contained.

[0031] the inside of the above-mentioned formula, and  $m -- 0.94 < m < 1.08$  -- it is  $0.970 \leq m \leq 1.030$  preferably. Producing semi-conductor-ization to baking under reducing atmosphere by making  $m$  larger than 0.94 is prevented, and even if it does not make burning temperature high by making  $m$  less than 1.08, a precise sintered compact can be obtained.

[0032] The range of  $m$  is  $0.94 < m < 1.08$ , and the point that the dielectric porcelain constituent of this invention differs from the conventional dielectric porcelain constituent has it in the point which carries out specified quantity addition of the 1st predetermined accessory constituent. By carrying out specified quantity addition of the 1st predetermined accessory constituent, even when low-temperature baking is

attained and lamination of the dielectric layer is carried out, without m of a principal component degrading the dielectric characteristics in the range of  $0.94 < m < 1.08$ , accelerated aging (elevated-temperature load life) of insulation resistance can be improved, and dependability can be improved sharply. Consequently, a miniaturization and high capacity-ization of a capacitor are attained.

[0033] In this invention, the 1st accessory constituent includes at least one or more kinds chosen from the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking. This 1st accessory constituent acts as matter which raises accelerated aging of insulation resistance while reducing sintering temperature. the ratio of the 1st accessory constituent [ as opposed to 100 mols of principal components at this invention ] -- the metallic element conversion in an oxide -- it is --  $0.01 \text{ mol} \leq$  -- the 1st -- accessory constituent  $< 2 \text{ mol}$  -- desirable --  $0.04 \text{ mol} \leq$  -- the 1st -- it is accessory constituent  $\leq 0.6 \text{ mol}$ . the ratio of the 1st accessory constituent -- the metallic element conversion in an oxide -- the  $0.01 \text{ mol} \leq$  1st accessory constituent --  $<$  -- m can improve accelerated aging of insulation resistance in the range of  $0.94 < m < 1.08$  by making it the range of two mols. As the 1st accessory constituent, it is V conversion and 0.04-mol or more content [ 0.6 mol or less extent ] of 0.01 mols or more the less than two mols of the compounds which turn into an oxide of V by the oxide of V and/or baking is carried out preferably. By making such 1st specific accessory constituent contain in the above-mentioned range, it is effective for improvement in an elevated-temperature load life.

[0034] Moreover, it is desirable to have added further the 2nd accessory constituent which contains the compound (for example,  $\text{MnCO}_3$ ) which turns into an oxide of Mn by the oxide (for example,  $\text{MnO}$ ) of Mn and/or baking in the dielectric porcelain constituent concerning this invention. It has the effectiveness which promotes sintering, and the effectiveness of improving an elevated-temperature load life, and, moreover, as for this 2nd accessory constituent, the effectiveness of reducing for example, the initial insulation resistance (IR) percent defective when carrying out lamination to about 4 micrometers also has a dielectric layer 2. the ratio of the 2nd accessory constituent to 100 mols of said principal components -- the metallic element conversion in an oxide -- it is --  $0 \text{ mol} \leq$  -- the 2nd -- accessory constituent  $< 4 \text{ mol}$  -- desirable --  $0.05 \text{ mol} \leq$  -- the 2nd -- it is accessory constituent  $\leq 1.4 \text{ mol}$ . the inclination that initial insulation resistance cannot be taken as the addition of the 2nd accessory constituent is four mols or more -- it is -- the addition of the 2nd accessory constituent --  $0 \text{ mol} \leq$  -- the 2nd -- in the range which is accessory constituent  $< 4 \text{ mol}$ , an elevated-temperature load life improves, moreover the outbreak of an initial IR percent defective can be reduced, so that there are many additions, and the rate of a capacity temperature change can be made small, so that there are few additions.

[0035] furthermore -- the dielectric porcelain constituent concerning this invention --  $\text{SiO}_2$  MO (however, at least one sort of elements with which M is chosen from Ba, calcium, Sr, and Mg),  $\text{Li}_2\text{O}$ , and B-2 O3 from -- it is desirable to have added further the 3rd accessory constituent containing at least one sort chosen. Although this 3rd accessory constituent acts mainly as sintering acid, it also has the effectiveness of improving the percent defective of the initial insulation resistance at the time of carrying out lamination (IR). From a viewpoint of a percent-defective improvement, it is  $\text{Li}_2$ . It is more desirable to make O contain. Moreover, from a viewpoint of a percent-defective improvement, it is  $\text{SiO}$  (Srp, calcium 1-p )3. It is more desirable to make it contain. in this case, p --  $0.3 \leq p \leq 1$  -- it is  $0.5 \leq p \leq 1$  preferably. Although p expresses Sr atomic number, it becomes possible by making the value of this p increase to raise the rate of an excellent article of the first stage IR of it.

[0036] the ratio of said 3rd accessory constituent to 100 mols of said principal components -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- accessory constituent  $< 15 \text{ mol}$  -- desirable --  $0.2 \text{ mol} \leq$  -- the 3rd -- it is accessory constituent  $\leq 6 \text{ mol}$ . By making [ more ] the addition of the 3rd accessory constituent than zero mol, it is effective for an improvement of a degree of sintering, and by making an addition into less than 15 mols, decline in specific inductive capacity is suppressed and sufficient capacity can be secured.

[0037] it is desirable to have added further the 4th accessory constituent which contains the oxide (however, R -- at least one element of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) of R in the dielectric porcelain constituent concerning this invention further again. This 4th

accessory constituent also has the effectiveness of improving the initial IR percent defective at the time of carrying out lamination besides [ which improves an elevated-temperature load life ] effectiveness. It is more desirable to make at least one oxide of Sc, Y, Ce, Dy, Ho, Er, Tm, Yb, and Lu contain from a viewpoint of this percent-defective improvement. the ratio of said 4th accessory constituent [ as opposed to / / when adding the 4th accessory constituent / 100 mols of said principal components ] -- R conversion in an oxide -- it is --  $0.02\text{mol} \leq$  -- the 4th -- accessory constituent  $< 2\text{ mol}$  -- desirable --  $0.02\text{mol} \leq$  -- the 4th -- it is accessory constituent  $\leq 0.6\text{ mol}$ .

[0038] In addition, what is necessary is just to determine suitably terms and conditions shown in drawing 1, such as the number of laminatings of a dielectric layer 2, and thickness, according to the purpose or an application. Moreover, a dielectric layer 2 consists of a grain and a grain boundary phase, and a certain thing is [ the mean particle diameter of the grain of a dielectric layer 2 ] desirable about 1-5 micrometers. This grain boundary phase usually uses as a component the oxide of the quality of the material which constitutes dielectric materials or an internal electrode ingredient, the oxide of the quality of the material added separately, and the oxide of the quality of the material mixed as an impurity still in process, and usually consists of glass thru/or glassiness.

[0039] Although especially the electric conduction material contained in the internal electrode layer 3 internal-electrode layer 3 is not limited, since the component of a dielectric layer 2 has reducibility-proof, base metal can be used for it. As a base metal used as electric conduction material, nickel or nickel alloy is desirable. As a nickel alloy, the alloy of one or more sorts of elements and nickel which are chosen from Mn, Cr, Co, and aluminum is desirable, and, as for nickel content in an alloy, it is desirable that it is 95 % of the weight or more. In addition, in nickel or nickel alloy, various minor constituents, such as P, Fe, and Mg, may be contained about 0.1 or less % of the weight. Although what is necessary is just to determine the thickness of an internal electrode layer suitably according to an application etc., it is usually especially desirable that it is about 1-2.5 micrometers 0.5-5 micrometers.

[0040] Although especially the electric conduction material contained in the external electrode 4 external electrode 4 is not limited, Cu, Cu alloy, nickel, nickel alloy, etc. are usually used for it. In addition, of course, Ag, an Ag-Pd alloy, etc. are usable. In addition, cheap nickel, Cu(s), and these alloys are used with this operation gestalt. Although the thickness of an external electrode should just be suitably determined according to an application etc., it is usually desirable that it is about 10-50 micrometers.

[0041] The stacked type ceramic condenser using the dielectric porcelain constituent of manufacture approach this invention of a stacked type ceramic condenser is manufactured by printing or imprinting and calcinating an external electrode, after producing the Green chip by usual print processes and the usual sheet method using a paste and calcinating this like the conventional stacked type ceramic condenser. Hereafter, the manufacture approach is explained concretely.

[0042] First, the paste for dielectric layers, the paste for internal electrodes, and the paste for external electrodes are manufactured, respectively.

[0043] The paste for paste dielectric layers for dielectric layers may be the coating of the organic system which kneaded the dielectric raw material and the organic vehicle, and may be the coating of a drainage system.

[0044] According to the presentation of the dielectric porcelain constituent concerning this invention mentioned above, the raw material which constitutes a principal component, and the raw material which constitutes the 1st - the 4th accessory constituent are used for a dielectric raw material. As a raw material which constitutes a principal component, the compound which turns into an oxide by the oxide of Sr, calcium, Ti, and Zr and/or baking is used. As a raw material which constitutes the 1st accessory constituent, one or more kinds of the single oxides or multiple oxides which are chosen from the compound which turns into these oxides are used after the oxide of V, Nb, W, Ta, and Mo, and/or baking. As a raw material which constitutes the 2nd accessory constituent, the single oxide or multiple oxide of a compound which turns into an oxide of Mn by the oxide of Mn and/or baking is used. as the raw material which constitutes the 3rd accessory constituent --  $\text{SiO}_2$  MO (however, at least one sort of elements with which M is chosen from Ba, calcium, Sr, and Mg), and  $\text{Li}_2\text{O}$  and  $\text{B}_2\text{O}_3$  from -- at least

one sort of compounds chosen are used. As a raw material which constitutes the 4th accessory constituent, the oxide (however, at least one sort as which R is chosen from Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) of R is used.

[0045] In addition, as a compound which turns into an oxide by baking, a carbonate, a nitrate, an oxalate, an organometallic compound, etc. are illustrated, for example. Of course, an oxide and the compound which turns into an oxide by baking may be used together. What is necessary is just to determine that the content of each compound in a dielectric raw material will serve as a presentation of the dielectric porcelain constituent described above after baking. As for these raw material powder, a thing with a mean particle diameter of about 0.0005-5 micrometers is usually used.

[0046] What is necessary is not to limit especially the binder that dissolves a binder into an organic solvent and is used for an organic vehicle, but just to choose it from the various usual binders, such as ethyl cellulose and a polyvinyl butyral, suitably with an organic vehicle. Moreover, what is necessary is not to limit especially the organic solvent used at this time, either, but just to choose from organic solvents, such as a terpeneol, butyl carbitol, an acetone, and toluene, suitably according to the approaches of using, such as print processes and the sheet method.

[0047] Moreover, what is necessary is to dissolve a water-soluble binder, a dispersant, etc. in water, not to limit especially an aqueous system binder but just to choose it from polyvinyl alcohol, a cellulose, water-soluble acrylic resin, an emulsion, etc. suitably with an aqueous system coating.

[0048] The paste for internal electrodes and the paste for paste internal electrodes for external electrodes knead the various oxide used as the electrical conducting material mentioned above after the electrical conducting material which consists of various conductive metals mentioned above or an alloy, or baking, an organometallic compound, resinate, etc. and the organic vehicle mentioned above, and are prepared. Moreover, the paste for external electrodes as well as this paste for internal electrodes is prepared.

[0049] What is necessary is not to limit especially the content of the organic vehicle of each paste mentioned above, but to make the usual content, for example, a binder, and just to make a solvent into about 10 - 50 % of the weight about 1 to 5% of the weight. Moreover, during each paste, the additive chosen from various dispersants, a plasticizer, a dielectric, an insulator, etc. if needed may contain.

[0050] When using print processes, laminating printing of a dielectric paste and the paste for internal electrodes is carried out on substrates, such as polyethylene terephthalate, and after cutting in a predetermined configuration, it considers as the Green chip by exfoliating from a substrate. On the other hand, when using the sheet method, after forming a green sheet using a dielectric paste and printing an internal electrode paste on this, the laminating of these is carried out and it considers as the Green chip.

[0051] Next, it de-binder-processes and this Green chip is calcinated.

[0052] A programming rate is made in 10-100 degrees C/hour, and 5-300 degrees C/hour of 180-400 degrees C of 200-300 degrees C and the temperature holding times are more preferably made [ in / although what is necessary is just to perform debinder processing debinder processing on condition that usual, when using base metal, such as nickel and nickel alloy, as electric conduction material of an internal electrode layer especially / an air ambient atmosphere ] into 5 - 20 hours for retention temperature for 0.5 to 24 hours.

[0053] the case where base metal, such as nickel and nickel alloy, is used as electric conduction material although what is necessary is just to determine the firing environments of a baking Green chip suitably according to the class of electric conduction material under paste for internal electrode layers -- the oxygen tension of a firing environments -- desirable -- 10-10 - ten to 3 Pa -- carrying out -- more -- desirable -- 10-10 - it is referred to as  $6 \times 10^{-5}$  Pa. If the oxygen tension at the time of baking is too low, the electric conduction material of an internal electrode will cause abnormality sintering, and will break off, and when oxygen tension is too high, there is a possibility that an internal electrode may oxidize. especially -- oxygen tension -- 10-10 - by adjusting to  $6 \times 10^{-5}$  Pa, it has the outstanding capacity temperature characteristic, moreover accelerated aging of insulation resistance can improve, and the dependability of the laminating mold ceramic condenser 1 obtained can be raised.

[0054] 1000-1400 degrees C of retention temperature of baking are 1200-1380 degrees C more

preferably. It is because eburnation will become inadequate if retention temperature is too low, the electrode by abnormality sintering of an internal electrode will break off if retention temperature is too high, or the capacity temperature characteristic gets worse by diffusion of the internal electrode quality of the material.

[0055] It is desirable to make 200-300 degrees C /and the temperature holding time an hour for 1 to 3 hours, to make more desirable 50-500 degrees C /of 50-500 degrees C /of cooling rates in 200-300 degrees C/hour an hour more preferably an hour, for 0.5 to 8 hours, and for a firing environments to make a programming rate a reducing atmosphere as baking conditions other than this, and it is desirable to humidify and use the mixed gas of nitrogen gas and hydrogen gas as a controlled atmosphere.

[0056] When it calcinates by the reducing atmosphere, it is desirable to give annealing (heat treatment) to the sintered compact of a capacitor chip.

[0057] Annealing (heat treatment) annealing is processing for reoxidating a dielectric layer, and, thereby, can make insulation resistance increase. 10 - 4 or more Pa of oxygen tension of an annealing ambient atmosphere is 10-1-10Pa more preferably. If oxygen tension is too low, reoxidation of a dielectric layer 2 will become difficult, and when oxygen tension is too high, there is a possibility that the internal electrode layer 3 may oxidize. It is much more effective for a defect incidence-rate improvement of initial insulation resistance (IR) by facing heat-treating the sintered compact which calcinates the dielectric porcelain constituent of this invention and is obtained especially, and adjusting oxygen tension to the range of 10-1-10Pa.

[0058] 1100 degrees C or less of retention temperature in the case of annealing are 500-1100 degrees C more preferably. When retention temperature is too low, reoxidating [ of a dielectric layer ] becomes inadequate, insulation resistance gets worse, and there is an inclination for the accelerated aging to also become short. Moreover, when retention temperature is too high, an internal electrode oxidizes, not only capacity falls, but it reacts with a dielectric base and there is an inclination for the capacity temperature characteristic, insulation resistance, and its accelerated aging to get worse. In addition, annealing can also consist of only a temperature up stroke and a temperature fall stroke. In this case, the temperature holding time is zero and retention temperature is synonymous with a maximum temperature.

[0059] It is desirable to make the temperature holding time for 6 to 10 hours, to make more desirable 50-500 degrees C /of cooling rates in 100-300 degrees C/hour an hour more preferably for 0 to 20 hours, and to humidify and use nitrogen gas as a controlled atmosphere of annealing as annealing conditions other than this, for example.

[0060] In addition, like baking mentioned above, in order to humidify nitrogen gas and mixed gas in said debinder processing and an annealing process, WETTA etc. can be used and, as for the water temperature in this case, it is desirable to consider as 5-75 degrees C.

[0061] Moreover, even if it carries out continuously, mutually-independent [ of these debinder processing, baking, and the annealing ] may be carried out, and they may be performed. It is more desirable to continue, to change an ambient atmosphere, to change an ambient atmosphere, if it calcinates by carrying out a temperature up, it cools continuously to the retention temperature in the case of baking and the retention temperature of annealing is reached, and to perform annealing treatment, without cooling after debinder processing, in performing these continuously. It is desirable to change an ambient atmosphere and to continue a temperature up further, after carrying out a temperature up under nitrogen gas or the humidified nitrogen-gas-atmosphere mind to the retention temperature at the time of debinder processing about baking on the other hand, in performing these independently, and after cooling to the retention temperature of annealing, it is desirable to change into nitrogen gas or the humidified nitrogen-gas-atmosphere mind again, and to continue cooling. Moreover, it is good also as a nitrogen-gas-atmosphere mind which could change the ambient atmosphere after carrying out a temperature up to retention temperature under nitrogen-gas-atmosphere mind about annealing, and humidified all the processes of annealing.

[0062] End-face polish is given with barrel finishing or sandblasting, it prints or imprints on the capacitor baking object acquired as mentioned above, the paste for external electrodes is calcinated on it, and the external electrode 4 is formed. As for the baking conditions of the paste for external electrodes,

it is desirable to consider as 10 minutes - about 1 hour at 600-800 degrees C for example, in the mixed gas of the nitrogen gas and hydrogen gas which were humidified. And an enveloping layer (pad layer) is formed in the front face of the external electrode 4 by plating etc. if needed.

[0063] Thus, by soldering etc., the ceramic condenser 1 of this manufactured operation gestalt is mounted on a printed circuit board, and is used for various electronic equipment.

[0064] Although the operation gestalt of this invention has been explained above, as for this invention, it is needless to say that it can carry out in the mode which becomes various within limits which are not limited to such an operation gestalt at all, and do not deviate from the summary of this invention.

[0065] For example, although the stacked type ceramic condenser was illustrated as electronic parts concerning this invention with the operation gestalt mentioned above, if it has the dielectric layer which it is not limited to a stacked type ceramic condenser, but is constituted from a dielectric porcelain constituent of the above-mentioned presentation as electronic parts concerning this invention, it is good anything.

[0066]

[Example] Next, the example which materialized the gestalt of operation of this invention more is given, and this invention is further explained to a detail. However, this invention is not limited only to these examples.

[0067] an example 1 -- the principal component raw material ( $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ) with a mean particle diameter of 0.1-1 micrometer, and the 1st - the 4th accessory constituent raw material were first prepared as a start raw material for producing dielectric materials, respectively. The oxide (the 1st accessory constituent:  $\text{V}_2\text{O}_5$  and 3rd accessory constituent:  $\text{SiO}_2 + \text{CaO}$  and 4th accessory constituent:  $\text{Y}_2\text{O}_3$ ) was used for other raw materials at the raw material of  $\text{MnO}$  using the carbonate (the 2nd accessory constituent:  $\text{MnCO}_3$ ). In addition,  $\text{SiO}_2$  which is the 3rd accessory constituent +  $\text{CaO}$  is  $\text{SiO}_2$ . And  $\text{CaSiO}_3$  obtained by carrying out wet blending of the  $\text{CaO}$  with a ball mill for 16 hours, calcinating in air at 1150 degrees C after desiccation, and carrying out wet grinding with a ball mill further for 100 hours The same property was acquired even if used.

[0068] These raw materials Empirical formula  $\{(\text{Sr}_{1-x}\text{Ca}_x)\text{O}\}_m - (\text{Ti}_{1-y}\text{Zr}_y)\text{O}_2$  (principal component) +  $\text{V}_2\text{O}_5$  (the 1st accessory constituent) +  $\text{MnCO}_3$  (the 2nd accessory constituent) +  $(\text{SiO}_2 + \text{CaO})$  (3rd accessory constituent) +  $\text{Y}_2\text{O}_3$  (the 4th accessory constituent) It sets. After carrying out weighing capacity so that the presentation after baking may become the compounding ratio shown in the samples 1-17 of Table 1 - 3, wet blending of these was carried out with the ball mill for about 16 hours, respectively, and the dielectric porcelain constituent (dielectric materials) was obtained by drying this.

[0069] Thus, the dielectric raw material 100 weight section after the obtained desiccation, the acrylic resin 4.8 weight section, the methylene chloride 40 weight section, the ethyl-acetate 20 weight section, the mineral spirit 6 weight section, and the acetone 4 weight section were mixed and pasted with the ball mill, and the paste for dielectric layers was obtained.

[0070] Subsequently, the nickel particle 100 weight section of 0.2-0.8 micrometers of mean diameters, the organic vehicle (what dissolved the ethyl cellulose 8 weight section in the butyl carbitol 92 weight section) 40 weight section, and the butyl carbitol 10 weight section were kneaded with 3 rolls, and were pasted, and the paste for internal electrode layers was obtained.

[0071] Subsequently, the Cu particle 100 weight section of 0.5 micrometers of mean diameters, and the organic vehicle (what dissolved the ethyl cellulose resin 8 weight section in the butyl carbitol 92 weight section) 35 weight section and the butyl carbitol 7 weight section were kneaded and pasted, and the paste for external electrodes was obtained.

[0072] Subsequently, after forming the green sheet with a thickness of 6 micrometers on the PET film using the above-mentioned paste for dielectric layers and printing the paste for internal electrode layers on this, the green sheet was exfoliated from the PET film. subsequently, these green sheets and the green sheet for protection (what does not print the paste for internal electrode layers) -- a laminating -- it was stuck by pressure and the Green chip was obtained. The number of laminatings of the sheet which has an internal electrode was made into four layers.

[0073] Subsequently, the Green chip was cut in predetermined size, debinder processing, baking, and



annealing (heat treatment) were performed, and the laminating ceramic baking object was acquired. Debinder processing was performed on condition that the air ambient atmosphere for the heating up time of 15 degrees C/hour, the retention temperature of 280 degrees C, and holding-time 8 hours. Moreover, baking is N<sub>2</sub> humidified the programming rate of 200 degrees C/hour, the retention temperature of 1200-1380 degrees C, holding-time 2 hours, and the cooling rate of 300 degrees C/hour. +H<sub>2</sub> It carried out on condition that the mixed-gas ambient atmosphere (oxygen tension is adjusted in  $2 \times 10^{-7}$  -  $5 \times 10^{-4}$  Pa). Annealing is N<sub>2</sub> humidified the retention temperature of 900 degrees C, temperature holding-time 9 hours, and the cooling rate of 300 degrees C/hour. It carried out on condition that the gas ambient atmosphere (oxygen tension is  $3.54 \times 10^{-2}$  to 2 Pa). In addition, WETTA which made water temperature 35 degrees C was used for baking and humidification of the controlled atmosphere in the case of annealing. [0074] Subsequently, N<sub>2</sub> which imprinted the paste for external electrodes to the end face, and humidified it after grinding the end face of a laminating ceramic baking object with sandblasting +H<sub>2</sub> Into the ambient atmosphere, it calcinated for 10 minutes at 800 degrees C, the external electrode was formed, and the sample of the stacked type ceramic condenser of a configuration of being shown in drawing 1 was obtained.

[0075] Thus, the size of each obtained sample was 3.2mmx1.6mmx0.6mm, the number of the dielectric layers pinched by the internal electrode layer was 4, the thickness was 4 micrometers, and the thickness of an internal electrode layer was 2 micrometers. The following property was evaluated about each sample.

[0076] Electrostatic capacity was measured with the digital LCR meter (4274 made from YHP A) with the base temperature of 25 degrees C to the sample of specific inductive capacity (epsilon<sub>n</sub>r) and an insulation resistance (IR) capacitor under the conditions of the frequency of 1kHz, and input signal level (measurement electrical potential difference) 1Vrms. And specific inductive capacity (with no unit) was computed from the obtained electrostatic capacity, and the electrode dimension of a capacitor sample and inter-electrode distance. Then, the insulation resistance IR after impressing DC50V to a capacitor sample for 60 seconds in 25 degrees C was measured using the insulation-resistance tester (Rby ADVANTEST CORP. 8340A), and it asked for specific resistance rho (a unit is ohm-cm) by count from this measured value, and the electrode surface product of a capacitor sample and thickness. A result is shown in Table 1 - 3. As evaluation, in order to create the small capacitor of a high dielectric constant, specific-inductive-capacity epsilon<sub>n</sub>r is an important property, and took 180 or more for it being more desirable and being [ 200 or more ] good. Resistivity made good more than  $1 \times 10^{12}$ -ohm-cm. The value of specific-inductive-capacity epsilon<sub>n</sub>r was calculated from the average of the value measured using the n= 10 sample number of capacitors. The value of specific resistance rho was made into the average of the specific resistance of ten excellent articles.

[0077] When the electrostatic capacity in the electrical potential difference of 1kHz and 1V is measured and reference temperature is made into 20 degrees C to the sample of the temperature characteristic capacitor of electrostatic capacity using an LCR meter, it investigates whether the electrostatic-capacity rate of change to temperature satisfies degree C in -2000-0 ppm /in a 20-85-degree C temperature requirement, and a result is shown in Table 1 - 3. Capacity rate-of-change \*\*C85/C20 (ppm/degree C) were computed by the following type 1.

\*\*C85/C20= {(C85-C20) /C20} x (1/65) -- Electrostatic capacity [ in / in C85 / 85 degrees C ] and C20 express the electrostatic capacity in 20 degrees C among a formula 1, however a formula 1.

[0078] Moreover, capacity rate-of-change deltaC/C in a -50 degrees C - +150 degrees C [ per typical sample 4 of this example ] temperature requirement was measured, and it graph-ized to drawing 2 . The rate of change on the basis of the capacity in 20 degrees C is expressed to this drawing. He can understand that the good capacity temperature characteristic is shown so that clearly also from this drawing.

[0079] The elevated-temperature load life was measured to the sample of an elevated-temperature load life (accelerated aging of insulation resistance) capacitor by holding in the impression condition with a direct current voltage of 8v [/micrometer ] at 175 degrees C. This elevated-temperature load life was performed about ten capacitor samples (thickness of 4 micrometers of a dielectric layer), and was



evaluated by measuring average-life time amount. A result is shown in Table 1 - 3. As evaluation, it becomes especially important [ life ], in case an elevated-temperature load life carries out lamination of the dielectric layer, and time amount until single figure resistance falls from impression initiation was defined as the life.

[0080] Moreover, V2 in the samples 3 and 4 (all are  $m=0.985$ ) which are the examples of this invention O5 The relation between an addition (V conversion) and an elevated-temperature load lifetime was shown in drawing 3 . As shown in this drawing, when the addition of V increases and it becomes 0.2 mols, a lifetime is an average of 184 hours, and is understood that the dependability of a capacitor is higher than the time with few additions. Moreover, compared with the addition of zero mol, it has checked that a life was improved by 2000 or more times. Furthermore, V2 in the samples 9-11 (all are  $m=1.02$ ) which are the examples of this invention O5 The relation between an addition (V conversion) and an elevated-temperature load lifetime was shown in drawing 4 . As shown in this drawing, when the addition of V increases and it becomes 0.2 mols, a lifetime is before or after an average of 23 hours, and is understood that the dependability of a capacitor is higher than the time with few additions. Moreover, compared with the addition of zero mol, it has checked that a life was improved by 2000 or more times.

[0081]

[Table 1]

表1

試料 番号		第1副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性	高温負荷 寿命 (時間)
		種類	モル				$\Delta C_{65}/C_{20}$ (ppm/°C)	
1	比較例	V	0	1300	235	1E+14	-738	0.08
2	実施例	V	0.01	1300	230	1.02E+14	-710	0.2
3	実施例	V	0.1	1300	247	1.13E+14	-720	4.2
4	実施例	V	0.2	1220	240	2.84E+13	-731	184
5	実施例	V	1.8	1220	225	3E+12	-780	763
6	比較例	V	2	1220	—*	—*	—*	—*

ただし、主成分の $m=0.985$

主成分の $x=0.36$ ,  $y=0$

第2副成分( $MnO_2$ )のMn換算のモル数=0.37モル

第3副成分( $SiO_2+CaO$ )のモル数=(0.4+0.4)モル

第4副成分( $Y_2O_3$ )のY換算のモル数=0.07モル

[\*]=半導体化

[0082]

[Table 2]

表2

試料 番号		第1副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性	高温負荷 寿命 (時間)
		種類	モル				$\Delta C_{65}/C_{20}$ (ppm/°C)	
7	比較例	V	0	1380	215	2E+13	-832	<0.01
8	実施例	V	0.01	1380	223	2.5E+13	-853	0.1
9	実施例	V	0.05	1380	220	4E+13	-850	0.35
10	実施例	V	0.1	1380	230	1E+14	-880	2.3
11	実施例	V	0.2	1380	210	5E+13	-890	23
12	実施例	V	1.8	1380	212	2E+12	-908	78
13	比較例	V	2	1380	—*	—*	—*	—*

ただし、主成分の $m=1.02$

主成分の $x=0.36$ ,  $y=0$

第2副成分( $MnCO_3$ )のMn換算のモル数=0.37モル

第3副成分( $SiO_2+CaO$ )のモル数=(2.5+2.5)モル

第4副成分( $Y_2O_3$ )のY換算のモル数=0モル

[\*]=半導体化

[0083]

[Table 3]

表3

試料 番号		主成分 m	焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性	高温負荷 寿命 (時間)
						$\Delta C_{45}/C_{20}$ (ppm/°C)	
14	比較例	0.94	1220	—*	—*	—*	—*
15	実施例	0.985	1200	214	1E+14	-534	129
16	実施例	1.02	1360	226	2E+14	-842	2.2
17	比較例	1.08	1380	—**	—**	—**	—**

ただし、主成分の $x=0.36$ 、 $y=0$

第1副成分( $V_2O_5$ )のV換算のモル数=0.1モル

第2副成分( $MnCO_3$ )のMn換算のモル数=0.37モル

第3副成分( $SiO_2+CaO$ )のモル数=(2.5+2.5)モル

第4副成分( $Y_2O_3$ )のY換算のモル数=0.07モル

「\*」=半導体化、「\*\*」=緻密化不可

[0084] The number of mols of the 1st - the 4th accessory constituent in Table 1 - 3 is a ratio to 100 mols of principal components. Moreover, in the numeric value of specific resistance ( $\rho$ ), "mE+n" means "mx10+n" among Table 1 - 3.

[0085] From the result shown in Table 1 - 2, the following things are understood about the addition of the 1st accessory constituent. If V is not added at all like a sample 1 and a sample 7, an elevated-temperature load lifetime is extremely short. Moreover, a dielectric is semi-conductor-ized as the addition of V is two mols like a sample 6 and a sample 13, and insulation resistance is inadequate. on the other hand, with the samples 2-5 which carry out specified quantity content, and the sample of 8-12, the 1st accessory constituent Have sufficient specific inductive capacity and insulation resistance, and it is not returned in baking by reducing atmosphere. Moreover, the nickel which is an internal electrode ingredient does not oxidize, either, it can check that the dielectric porcelain constituent excellent in reducibility-proof is obtained, and the capacity temperature characteristic is excellent, and it has checked that an elevated-temperature load life (accelerated aging of insulation resistance) could moreover be improved. V2O5 It replaces with and is MoO3. WO3 Ta2 O5 And Nb2 O5 Although it added, respectively and the same conditions as the above estimated, respectively, the result with the almost same all was obtained. In addition, samples 2-5 and samples 8-12 show the example of this invention, and samples 1, 6, 7, and 13 show the example of a comparison of this invention.

[0086] From the result shown in Table 3, the following things are understood about the ratio of m of a principal component. Like a sample 14, in the case of  $m=0.94$ , the dielectric was able to be returned by baking under reducing atmosphere, and sufficient insulation resistance could not be taken, but it has checked not acting as a capacitor. Moreover, even if it carries out specified quantity content of the 1st accessory constituent to it being  $m=1.08$  like a sample 17, and it calcinates at 1380 degrees C (elevated temperature), a precise sintered compact is not obtained. In addition, samples 15 and 16 show the example of this invention, and samples 14 and 17 show the example of a comparison of this invention.

[0087]  $m=1.02$  of example 2 principal component,  $x=0.36$ ,  $y=0$ , the number of mols of the 1st accessory constituent (V) = 0.1 mols, the mol of the 3rd accessory constituent ( $SiO_2 + CaO$ ) -- a number -- = (2.5+2.5) mol and the mol of (Y) of the 4th accessory constituent -- except for having considered as =0.07 mol the number --  $MnCO_3$  as the 2nd accessory constituent The addition (Mn conversion) was changed as shown in Table 4, and it was evaluated. A result is shown in Table 4.

[0088]

[Table 4]

表4

試料 番号		第2副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性	高温負荷 寿命 (時間)	初期IR 不良率 (%)
		種類	モル				$\Delta C_{25}/C_{20}$ (ppm/°C)		
18	実施例	Mn	0	1380	215	8.5E+12	-610	0.02	90
19	実施例	Mn	0.05	1380	217	9.62E+12	-625	0.1	82
20	実施例	Mn	0.37	1380	226	2E+14	-841	2.2	23
21	実施例	Mn	0.73	1380	221	6.88E+13	-1236	13	10
22	実施例	Mn	1.5	1380	210	2E+13	-1676	20	7
23	実施例	Mn	3.8	1380	205	1.3E+12	-1846	32	8
24	比較例	Mn	4	1380	198	<1E+12	-1994	×	×

ただし、主成分の $m=1.02$ 主成分の $x=0.36, y=0$ 第1副成分( $V_2O_5$ )のV換算のモル数=0.1モル第3副成分( $SiO_2+CaO$ )のモル数=(2.5+2.5)モル第4副成分( $Y_2O_3$ )のY換算のモル数=0.07モル

[0089] as shown in Table 4, the addition of the 2nd accessory constituent (Mn conversion) is four mols - initial insulation resistance -- falling -- the addition of the 2nd accessory constituent -- 0mol<= -- the 2nd -- in the range which is accessory constituent <4 mol The elevated-temperature load life (accelerated aging of insulation resistance) was able to improve as there being many additions (3.8 mols), moreover the outbreak of an initial IR percent defective could also be reduced, and it has checked that the rate of a capacity temperature change became small in that there are few additions (zero mol).

[0090] In addition, the value of an initial IR percent defective asked for the specific resistance  $\rho$  of about 100 capacitor samples by count, respectively from the thickness (this example 4 micrometers) of insulation resistance IR, an electrode surface product, and a dielectric layer, divided the number of a sample smaller single or more figures than the value of the specific resistance  $\rho$  at the time of the condition of bulk by the whole number, and showed it at the percentage. An initial IR percent defective will be so low that this value is small, and there will be many excellent articles.

[0091] Moreover, capacity rate-of-change  $\Delta C/C$  in a sample 19 and a -50 degrees C - +150 degrees C [ per 20 ] temperature requirement was measured, and it graph-ized to drawing 5. The rate of change on the basis of the capacity in 20 degrees C is expressed to this drawing. As shown in this drawing, it can check that all of samples 19 and 20 show the good capacity temperature characteristic.

[0092] In addition,  $MnCO_3$  Although it replaced with,  $MnO$  was added and the same conditions as the above estimated, respectively, the result with the same all was obtained.

the mol of  $m=0.985$  of example 3 principal component,  $x=0.36, y=0$ , and the 1st accessory constituent (V conversion) -- number = -- 0.2 mols the mol of the 2nd accessory constituent (Mn conversion) -- a number -- =0.37 mol and the mol of (Y conversion) of the 4th accessory constituent -- besides having considered as =0.07 mol the number, the addition of ( $SiO_2+CaO$ ) as the 3rd accessory constituent was changed as shown in Table 5, and extent of an improvement of an elevated-temperature load life was examined. A result is shown in Table 5.

[0093]

[Table 5]

表5

試料 番号		第3副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega\text{cm}$ )	容量温度特性 $\Delta C_{10}/C_{20}$ (ppm/°C)	高温負荷 寿命 (時間)	初期IR 不良率 (%)
		種類	モル						
4-1	比較例	SiO <sub>2</sub> +CaO	0	1380	—**	—**	—**	—**	—**
4	実施例	SiO <sub>2</sub> +CaO	0.4+0.4	1220	240	2.84E+13	-731	184	84
4-2	実施例	SiO <sub>2</sub> +CaO	2.5+2.5	1220	218	3.73E+13	-853	220	72
4-3	実施例	SiO <sub>2</sub> +CaO	4+4	1220	222	3.5E+13	-873	232	75
4-4	実施例	SiO <sub>2</sub> +CaO	5+5	1220	183	2.6E+13	-808	166	73
4-5	実施例	SiO <sub>2</sub> +CaO	6.8+6.8	1220	182	8E+12	-987	135	88
4-6	比較例	SiO <sub>2</sub> +CaO	7.5+7.5	1220	175	2E+12	-1035	98	85

ただし、主成分のm=0.985

主成分のx=0.36、y=0

第1副成分(Y<sub>2</sub>O<sub>3</sub>)のY換算のモル数=0.2モル第2副成分(MnCO<sub>3</sub>)のMn換算のモル数=0.37モル第4副成分(Y<sub>2</sub>O<sub>3</sub>)のY換算のモル数=0.07モル

「\*\*」=測定不可

[0094] As shown in Table 5, the degree of sintering has been improved by making [ more ] the addition of the 3rd accessory constituent than zero mol. By making an addition into less than 15 mols, decline in specific inductive capacity was suppressed and it has checked that sufficient capacity was also securable. In addition, the value of an initial IR percent defective was calculated like the example 2. In addition, it is CaSiO<sub>3</sub> instead of (SiO<sub>2</sub> +CaO). The same result was obtained even if used.

[0095] Except having changed the thickness of example 4 dielectric layer, as shown in drawing 6, two or more capacitor samples were produced like the sample 20 of the example 2 shown in Table 4 (sample 25). Moreover, it is SiO<sub>2</sub> as the 3rd accessory constituent. It used and two or more capacitor samples were produced like the sample 20 of the example 2 shown in Table 4 except having changed the thickness of a dielectric layer, as shown in drawing 6 (sample 26). The trial which checks the effect which it has on initial insulation resistance (IR) when the class of the 3rd accessory constituent carries out lamination of the dielectric layer was performed using these capacitor samples. Although the result was shown in drawing 6, as shown also in this drawing, it has checked that the variation in initial insulation resistance (IR) had little direction which used (SiO<sub>2</sub> +CaO) as the 3rd accessory constituent also to the lamination of a dielectric layer. In addition, it is CaSiO<sub>3</sub> instead of (SiO<sub>2</sub> +CaO). The same result was obtained even if used.

[0096] Except having changed the thickness of example 5 dielectric layer with 7 micrometers or more, 4 micrometers, and 2 micrometers Two or more capacitor samples are produced like the sample 20 of the example 2 shown in Table 4 (samples 27-29). Moreover, it is Li<sub>2</sub> further to (SiO<sub>2</sub> +CaO) as the 3rd accessory constituent. Except having added 1.4 mols O and having changed the thickness of a dielectric layer with 7 micrometers or more, 4 micrometers, and 2 micrometers Two or more capacitor samples were produced like the sample 20 of the example 2 shown in Table 4 (samples 30-32), and the defect incidence rate of the initial insulation resistance (IR) of these samples was computed. It is Li<sub>2</sub> as it becomes thin with 4 micrometers and 2 micrometers although a defect incidence rate is not affected (refer to drawing 7 (A)) when thickness is as thick as 7 micrometers or more even if it adds Li<sub>2</sub>O, although a result is shown in drawing 7 (A) - drawing 7 (C). It has checked that the effectiveness of O addition appeared (refer to drawing 7 (B) - (C)). In addition, the value of an initial IR percent defective was calculated like the example 2.

[0097] Except having made the addition of the example 6 3rd accessory constituent (SiO<sub>2</sub> +CaO) into 5.0 mols, the capacitor sample was produced like the sample 3 of the example 1 shown in Table 1 (sample 33). Moreover, Y as the 4th accessory constituent was not added, but the capacitor sample was produced like the sample 3 of the example 1 shown in Table 1 except having made the addition of the 3rd accessory constituent (SiO<sub>2</sub> +CaO) into 5.0 mols (sample 34). The existence of addition of Y as the 4th accessory constituent performed the trial for checking the effect which it has on an elevated-temperature load life (accelerated aging of insulation resistance) using these capacitor samples. Although the result was shown in drawing 8, as shown also in this drawing, it has checked that the direction which added Y could improve an elevated-temperature load life.

[0098] About the oxygen tension in example 7 heat treatment process, it is  $3.54 \times 10$  to 2 Pa (900 degrees C). 9 hours, UETTA temperature of 35 degrees C,  $4.23 \times 10$  to 1 Pa (1100 degrees C) Except having considered as the UETTA temperature of 35 degrees C, and having changed the thickness of a dielectric layer with 9 micrometers (samples 35-36) and 4 micrometers (samples 37-38) for 3 hours Two or more samples were produced like the sample 4 of the example 1 shown in Table 1, and the defect incidence rate of the initial insulation resistance (IR) of these samples was computed. Although a result is shown in drawing 9 (A) - drawing 9 (B) When the thickness of a dielectric layer is as thick as 9 micrometers, the difference in oxygen tension does not affect a defect incidence rate, but (refer to drawing 9 (A)) if it becomes thin with 4 micrometers It has checked that the effectiveness at the time of adjusting oxygen tension to  $4.23 \times 10$  to 1 Pa (sample 38) which is 10 - 4 or more (it is incidentally also within the limits of 10-1-10Pa) Pa appeared (refer to drawing 9 (B)). The value of an initial IR percent defective was calculated like the example 2. Although the oxygen tension in a heat treatment process was set to  $9.61 \times 10$  to 2 Pa (1100 degrees C, 3 hours, UETTA temperature of 0 degree C) and the effectiveness of reduction of the outbreak of a percent defective of initial insulation resistance was checked in addition like samples 35-36 and samples 37-38 (samples 39-40 and especially effectiveness such were not checked.) It is thought that the retention temperature at the time of heat treatment has not contributed to reduction of the defect incidence rate of the initial insulation resistance of a sample, and the oxygen tension at the time of heat treatment has contributed from this.

[0099] The example 8 3rd accessory constituent = ( $\text{SiO}_2 + \text{CaO}$ ) ( $0.4 + 0.4$ ) mol ( $p = 0$ ), = ( $0.4 + 0.2 + 0.2$ ) mol ( $p = 0.5$ ), ( $\text{SiO}_2 + \text{CaO} + \text{SrO}$ ) And ( $\text{SiO}_2 + \text{SrO}$ ) it considers as = ( $0.4 + 0.4$ ) mol ( $p = 1$ ). and annealing -- the retention temperature of 1100 degrees C, and the temperature holding time --  $\text{N}_2$  humidified for 3 hours Two or more capacitor samples were produced like the sample 4 except having carried out in the gas ambient atmosphere (oxygen tension being  $4.23 \times 10$  to 1 Pa) (samples 41, 42, and 43). And  $\text{SiO}_3$  as the 3rd accessory constituent (Srp, calcium 1-p) It set and the content rate of Sr evaluated what kind of effect it would have on the rate of an excellent article of the initial insulation resistance (IR) in a capacitor sample. A result is shown in drawing 10. It has checked that the rate of an excellent article of the first stage IR improved with 75% (sample 41), 83% (sample 42), and 100% (sample 43), namely, the percent defective of the first stage IR fell with 25%, 17%, and 0% from the result shown in drawing 10, so that the content rate of Sr increases. In addition, the value of the percent defective of the first stage IR was calculated like the example 2.

[0100]

[Effect of the Invention] As explained above, according to this invention, it has the capacity temperature characteristic which was excellent in the reducibility-proof at the time of baking, and was excellent after baking, and the dielectric porcelain constituent which can moreover raise accelerated aging of insulation resistance can be offered. Moreover, according to this invention, it has the outstanding capacity temperature characteristic, moreover accelerated aging of insulation resistance can improve, and electronic parts, such as a chip capacitor with which dependability was raised, can be offered. Furthermore, according to this invention, the manufacture approach of electronic parts that the outbreak of the percent defective of initial insulation resistance is improvable can also be offered, maintaining the dependability for which electronic parts are asked.

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to electronic parts using the dielectric porcelain constituent used as a dielectric layer of for example, a laminating mold ceramic condenser etc., and its dielectric porcelain constituent as a dielectric layer, and its manufacture approach.

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PRIOR ART

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[Description of the Prior Art] The laminating mold ceramic condenser which is an example of electronic parts carries out the laminating of the green sheet of two or more sheets which printed conductive paste on the green sheet which consists of a predetermined dielectric porcelain constituent, and printed this conductive paste, calcinates a green sheet and an internal electrode in one, and is formed.

[0003] When the conventional dielectric porcelain constituent was calcinated under the neutrality which is a hypoxia partial pressure, or a reducing atmosphere, it was returned and it had the semi-conductor-ized property. For this reason, it was obliged to face manufacturing a laminating mold ceramic condenser and to calcinate under the oxidizing atmosphere which is a hyperoxia partial pressure. In connection with this, it did not need to fuse as a dielectric porcelain constituent and an internal electrode ingredient calcinated by coincidence at the temperature which this dielectric porcelain constituent sinters, but the expensive noble metals (for example, palladium, platinum, etc.) which do not oxidize even if it calcinates under an oxidizing quality ambient atmosphere needed to be used, and it had become big hindrance to low-pricing of the laminating mold ceramic condenser manufactured.

[0004] On the other hand, in order to use cheap base metal (for example, nickel, copper, etc.) as an ingredient of an internal electrode, it is required to develop the dielectric porcelain constituent which does not semi-conductor-ize even if it calcinates at low temperature under neutrality or a reducing atmosphere, namely, is excellent in reducibility-proof, and has specific inductive capacity sufficient after baking and outstanding dielectric characteristics (for example, the rate of a capacity temperature change is small).

[0005] Conventionally, various proposals are made as a dielectric porcelain constituent which can use base metal as an ingredient of an internal electrode.

[0006] for example, in JP,63-224108,A ( $\text{Sr}_{1-x}\text{Ca}_x$ )<sub>m</sub> ( $\text{Ti}_{1-y}\text{Zr}_y$ )<sub>3</sub> The dielectric oxide of the presentation shown Use ( $0.30 \leq x \leq 0.50$ ,  $0.03 \leq y \leq 0.20$ ,  $0.95 \leq m \leq 1.08$ ) as a principal component, and this principal component 100 weight section is received. [ however, ] As an accessory constituent, it is Mn MnO<sub>2</sub> It is the 0.01 - 2.00 weight section and SiO<sub>2</sub> by conversion. The dielectric porcelain constituent which carries out 0.10-4.00 weight section content is indicated.

[0007] Moreover, at JP,63-224109,A, it is said Mn and SiO<sub>2</sub> to said principal component. In addition, the dielectric porcelain constituent which carries out 0.01-1.00 weight section content of the ZnO further is indicated.

[0008] Furthermore, at JP,4-206109,A, it is m ( $\text{Sr}_{1-x}\text{Ca}_x$ ) ( $\text{Ti}_{1-y}\text{Zr}_y$ )<sub>3</sub>. The dielectric porcelain constituent which uses the dielectric oxide (however,  $0.30 \leq x \leq 0.50$ ,  $0.00 \leq y \leq 0.20$ ,  $0.95 \leq m \leq 1.08$ ) of the presentation shown as a principal component, and has made the powder particle size the range of 0.1-1.0 micrometers is indicated.

[0009] Further again in JP,62-24388,B (MeO)<sub>k</sub> Use as a principal component the dielectric oxide (however, the metal and k as which Me was chosen from Sr, calcium, and Sr+calcium 1.00-1.04) of the presentation shown by TiO<sub>2</sub>, and this principal component 100 weight section is received. As a glass component, it is Li<sub>2</sub>. The dielectric porcelain constituent which carries out 0.2-10.0 weight section content of what used O, M (however, at least one sort of metallic oxides with which M is chosen from



BaO, CaO, and SrO), and SiO<sub>2</sub> by the predetermined mole ratio is indicated.

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EFFECT OF THE INVENTION

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[Effect of the Invention] As explained above, according to this invention, it has the capacity temperature characteristic which was excellent in the reducibility-proof at the time of baking, and was excellent after baking, and the dielectric porcelain constituent which can moreover raise accelerated aging of insulation resistance can be offered. Moreover, according to this invention, it has the outstanding capacity temperature characteristic, moreover accelerated aging of insulation resistance can improve, and electronic parts, such as a chip capacitor with which dependability was raised, can be offered. Furthermore, according to this invention, the manufacture approach of electronic parts that the outbreak of the percent defective of initial insulation resistance is improvable can also be offered, maintaining the dependability for which electronic parts are asked.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, in a dielectric porcelain constituent given [ these ] in an official report, all, accelerated aging of the insulation resistance after baking was short, and when the laminating mold ceramic condenser which has internal electrodes made from base metal, such as nickel, using this dielectric porcelain constituent was manufactured, there was a problem that the dependability of the laminating mold ceramic condenser obtained became low.

[0011] The purpose of this invention has the capacity temperature characteristic which was excellent in the reducibility-proof at the time of baking, and was excellent after baking, and is to offer the dielectric porcelain constituent which can moreover raise accelerated aging of insulation resistance. Moreover, the purpose of this invention is offering electronic parts, such as a chip capacitor with which it has the outstanding capacity temperature characteristic, accelerated aging of insulation resistance moreover improved, and dependability's was raised. Furthermore, the purpose of this invention is offering the manufacture approach of electronic parts the outbreak of the percent defective of initial insulation resistance being improvable, maintaining the dependability for which electronic parts are asked.

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MEANS

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[Means for Solving the Problem] In order to attain the above-mentioned purpose, the dielectric porcelain constituent concerning this invention  $\{(Sr_{1-x}Ca_x)O\}_m-(Ti_{1-y}Zr_y)O_2$  The principal component containing the dielectric oxide of the presentation shown, It is the dielectric porcelain constituent which has at least the 1st accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking. The notations  $mx$  and  $y$  which show the presentation mole ratio in the formula contained in said principal component the ratio of said 1st accessory constituent [ as opposed to / have the relation of  $0.94 < m < 1.08$ ,  $0 \leq x \leq 1.00$ , and  $0 \leq y \leq 0.20$ , and / 100 mols of said principal components ] -- the metallic element conversion in an oxide --  $0.01 \text{ mol} \leq$  -- the 1st -- it is characterized by being accessory constituent  $< 2 \text{ mol}$ .

[0013] the ratio of said 2nd accessory constituent [ as opposed to / the dielectric porcelain constituent concerning this invention has further preferably the 2nd accessory constituent containing the compound which turns into an oxide of Mn by the oxide of Mn, and/or baking, and / 100 mols of said principal components ] -- the metallic element conversion in an oxide --  $0 \text{ mol} \leq$  -- the 2nd -- it is accessory constituent  $< 4 \text{ mol}$ .

[0014] the dielectric porcelain constituent preferably applied to this invention --  $SiO_2$  MO (however, at least one sort of elements with which M is chosen from Ba, calcium, Sr, and Mg), and  $Li_2O$  and  $B_2O_3$  from -- the ratio of said 3rd accessory constituent [ as opposed to / have further the 3rd accessory constituent containing at least one sort chosen, and / 100 mols of said principal components ] -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- it is accessory constituent  $< 15 \text{ mol}$ . It is thought that the 3rd accessory constituent functions as sintering acid.

[0015] Especially the desirable mode of the 3rd accessory constituent is as being shown below. the dielectric porcelain constituent more preferably applied to this invention --  $SiO(Sr_p, \text{calcium}_{1-p})_3$  (however,  $p \ 0.3 \leq p \leq 1$ ) the ratio of said 3rd accessory constituent [ as opposed to / have the 3rd included accessory constituent further and / 100 mols of said principal components ] -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- it is accessory constituent  $< 15 \text{ mol}$ . It is thought that this kind of the 3rd accessory constituent functions as sintering acid.

[0016] Preferably,  $-2000-0 \text{ ppm } (^{\circ}C) / \text{of } -1500-0 \text{ ppm /of electrostatic-capacity rate of change [ as opposed to temperature in the dielectric porcelain constituent concerning this invention ] are [ } ^{\circ}C / ^{\circ}C ] -1000-0 \text{ ppm/} ^{\circ}C$  in an at least  $20-85-^{\circ}C$  temperature requirement. However, the reference temperature of electrostatic capacity  $C$  is  $20 ^{\circ}C$ .

[0017] In order to attain the above-mentioned purpose, the electronic parts concerning this invention are electronic parts which have a dielectric layer, and said dielectric layer is characterized by constituting from a dielectric porcelain constituent of one of the above.

[0018] Preferably, the electronic parts concerning this invention have the capacitor element body with which the laminating of the internal electrode layer has been carried out by turns with said dielectric layer.

[0019] Preferably, the electric conduction material by which the electronic parts concerning this invention are contained in said internal electrode layer is nickel or a nickel alloy.

[0020] In order to attain the above-mentioned purpose, the manufacture approach of the electronic parts concerning this invention The process which produces a dielectric paste using the dielectric porcelain constituent of one of the above, The process which produces the paste for internal electrodes, and the process which carries out the laminating of said dielectric paste and the paste for internal electrodes by turns, and obtains a layered product, It has the baking process which calcinates said layered product and obtains a sintered compact, and the process at which oxygen tension heat-treats preferably  $10^{-4}$  or more Pa of said sintered compact under a  $10^{-1}$ - $10^0$ Pa ambient atmosphere.

[0021] the manufacture approach of the electronic parts preferably built over this invention -- said baking process -- setting -- said layered product -- oxygen tension --  $10^{-1}$ - $10^0$  - it calcinates under the ambient atmosphere which is ten to 3 Pa.

[0022] Preferably, the manufacture approach of the electronic parts concerning this invention uses nickel or a nickel alloy as said paste for internal electrodes. In addition,  $\text{SiO}_2$  contained in the 3rd accessory constituent in the dielectric porcelain constituent concerning this invention  $\text{MO}$ ,  $\text{Li}_2\text{O}$ ,  $\text{B}_2\text{O}_3$  And (Srp , calcium1-p )  $\text{SiO}_3$  At least, each is the meaning which should just be such a presentation after baking, and also contains the compound which turns into these oxides after baking.

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OPERATION

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[Function] In the dielectric porcelain constituent concerning this invention, while having the capacity temperature characteristic which was excellent in the reducibility-proof at the time of baking, and was excellent after baking to the principal component containing the dielectric oxide of a specific presentation by carrying out specified quantity addition of the 1st specific accessory constituent, compared with the case where the 1st accessory constituent is not added, accelerated aging of insulation resistance improves more than 1000 times (for example, 175 degrees C, DC8v/micrometer).

[0024] Since it has the dielectric layer constituted from electronic parts, such as a chip capacitor concerning this invention, with the dielectric porcelain constituent concerning this invention, it has the outstanding capacity temperature characteristic (for example, the SL property of JIS is satisfied), moreover accelerated aging of insulation resistance improves, and the dependability of electronic parts improves.

[0025] By the manufacture approach of the electronic parts concerning this invention, the outbreak of the percent defective of initial insulation resistance is efficiently improvable, maintaining the dependability for which electronic parts, such as a chip capacitor, are asked by having the process at which oxygen tension heat-treats the sintered compact obtained by baking under the ambient atmosphere of 10<sup>-4</sup> or more Pa.

[0026]

[Embodiment of the Invention] Hereafter, this invention is explained based on the operation gestalt shown in a drawing. The sectional view of the stacked type ceramic condenser which drawing 1 requires for 1 operation gestalt of this invention, The graph which shows the capacity temperature characteristic of the sample 4 whose drawing 2 is the example of this invention, the graph which shows the relation of the addition of V and elevated-temperature load lifetime in the samples 3 and 4 whose drawing 3 is the examples of this invention, The graph which shows the relation of the addition of V and elevated-temperature load lifetime in the samples 9-11 whose drawing 4 is the examples of this invention, When the thickness of a dielectric layer is replaced with, the graph and drawing 7 which show the relation between the thickness of a dielectric layer when the graph and drawing 6 which show the capacity temperature characteristic of the samples 19 and 20 whose drawing 5 is the examples of this invention replace the class of the 3rd accessory constituent with, and initial insulation resistance When the thickness of a dielectric layer is replaced with, the graph which shows the relation between the existence of Li addition, and the percent defective of initial insulation resistance, the graph with which drawing 8 shows the existence of addition of Y as the 4th accessory constituent, and relation with an elevated-temperature load life, and drawing 9 the graph and drawing 10 which show the relation between the oxygen tension in a heat treatment process, and the percent defective of initial insulation resistance -- SiO (Srp, calcium 1-p)<sub>3</sub> as the 3rd accessory constituent setting -- content of Sr -- it is the graph which shows relation with the rate of an excellent article of the initial insulation resistance (IR) of a capacitor sample comparatively.

[0027] As shown in stacked type ceramic condenser drawing 1, the stacked type ceramic condenser 1 as electronic parts concerning 1 operation gestalt of this invention has the capacitor element body 10 of a

configuration of that the laminating of a dielectric layer 2 and the internal electrode layer 3 was carried out by turns. The external electrode 4 of the internal electrode layer 3 arranged by turns inside the component body 10 and the pair through which it flows respectively is formed in the both ends of this capacitor element body 10. Although there is especially no limit in the configuration of the capacitor element body 10, it usually considers as the shape of a rectangular parallelepiped. Moreover, although what is necessary is for there to be especially no limit also in the dimension, and just to consider as a suitable dimension according to an application, it is usually  $x(0.6-5.6\text{mm}) (0.3-5.0\text{mm}) \times (0.3-1.9\text{mm})$  extent. The laminating of the internal electrode layer 3 has been carried out so that each end face may be exposed to the front face of two edges where the capacitor element body 10 counters by turns. It is formed in the both ends of the capacitor element body 10, it connects with the exposure end face of the internal electrode layer 3 arranged by turns, and the external electrode 4 of a pair constitutes a capacitor circuit.

[0028] Dielectric layer 2 dielectric layer 2 contains the dielectric porcelain constituent of this invention. The dielectric porcelain constituent of this invention is  $\{(Sr_{1-x}Ca_x)O\}_m \cdot (Ti_{1-y}Zr_y)O_2$  It has the 1st accessory constituent including one or more kinds chosen from the principal component containing the dielectric oxide of the presentation shown, and the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking at least. Under the present circumstances, the amount of oxygen (O) may be deflected from the stoichiometric composition of the above-mentioned formula a little.

[0029] the inside of the above-mentioned formula, and  $x -- 0 \leq x \leq 1.00 --$  it is  $0.30 \leq x \leq 0.50$  preferably.  $x$  expresses calcium atomic number and it becomes possible to shift the phase transition point of a crystal to arbitration by changing  $x$ , i.e., a calcium/Sr ratio. Therefore, a capacity temperature coefficient and specific inductive capacity are controllable to arbitration. If  $x$  is made into the above-mentioned range, the phase transition point of a crystal can exist near a room temperature, and the temperature characteristic of electrostatic capacity can be raised. However, in this invention, the ratio of Sr and calcium is arbitrary and may contain only one side.

[0030] the inside of the above-mentioned formula, and  $y -- 0 \leq y \leq 0.20 --$  it is  $0 \leq y \leq 0.10$  preferably. Decline in specific inductive capacity is prevented by making  $y$  or less into 0.20.  $y$  is  $TiO_2$  although Zr atomic number is expressed.  $ZrO_2$  which compares and is hard to be returned There is an inclination which reducibility-proof increases further by permuting. However, in this invention, Zr does not necessarily need to be included and only Ti may be contained.

[0031] the inside of the above-mentioned formula, and  $m -- 0.94 < m < 1.08 --$  it is  $0.970 \leq m \leq 1.030$  preferably. Producing semi-conductor-ization to baking under reducing atmosphere by making  $m$  larger than 0.94 is prevented, and even if it does not make burning temperature high by making  $m$  less than 1.08, a precise sintered compact can be obtained.

[0032] The range of  $m$  is  $0.94 < m < 1.08$ , and the point that the dielectric porcelain constituent of this invention differs from the conventional dielectric porcelain constituent has it in the point which carries out specified quantity addition of the 1st predetermined accessory constituent. By carrying out specified quantity addition of the 1st predetermined accessory constituent, even when low-temperature baking is attained and lamination of the dielectric layer is carried out, without  $m$  of a principal component degrading the dielectric characteristics in the range of  $0.94 < m < 1.08$ , accelerated aging (elevated-temperature load life) of insulation resistance can be improved, and dependability can be improved sharply. Consequently, a miniaturization and high capacity-ization of a capacitor are attained.

[0033] In this invention, the 1st accessory constituent includes at least one or more kinds chosen from the compound which turns into these oxides after the oxide of V, Nb, W, Ta, and Mo, and/or baking. This 1st accessory constituent acts as matter which raises accelerated aging of insulation resistance while reducing sintering temperature. the ratio of the 1st accessory constituent [ as opposed to 100 mols of principal components at this invention ] -- the metallic element conversion in an oxide -- it is --  $0.01\text{mol} \leq --$  the 1st -- accessory constituent  $< 2\text{ mol} --$  desirable --  $0.04\text{mol} \leq --$  the 1st -- it is accessory constituent  $\leq 0.6\text{ mol}$ . the ratio of the 1st accessory constituent -- the metallic element conversion in an oxide -- the  $0.01\text{ mol} \leq$  1st accessory constituent --  $< -- m$  can improve accelerated



aging of insulation resistance in the range of  $0.94 < m < 1.08$  by making it the range of two mols. As the 1st accessory constituent, it is V conversion and 0.04-mol or more content [ 0.6 mol or less extent ] of 0.01 mols or more the less than two mols of the compounds which turn into an oxide of V by the oxide of V and/or baking is carried out preferably. By making such 1st specific accessory constituent contain in the above-mentioned range, it is effective for improvement in an elevated-temperature load life.

[0034] Moreover, it is desirable to have added further the 2nd accessory constituent which contains the compound (for example,  $\text{MnCO}_3$ ) which turns into an oxide of Mn by the oxide (for example,  $\text{MnO}$ ) of Mn and/or baking in the dielectric porcelain constituent concerning this invention. It has the effectiveness which promotes sintering, and the effectiveness of improving an elevated-temperature load life, and, moreover, as for this 2nd accessory constituent, the effectiveness of reducing for example, the initial insulation resistance (IR) percent defective when carrying out lamination to about 4 micrometers also has a dielectric layer 2. the ratio of the 2nd accessory constituent to 100 mols of said principal components -- the metallic element conversion in an oxide -- it is --  $0\text{mol} \leq$  -- the 2nd -- accessory constituent  $< 4\text{ mol}$  -- desirable --  $0.05\text{mol} \leq$  -- the 2nd -- it is accessory constituent  $\leq 1.4\text{ mol}$ . the inclination that initial insulation resistance cannot be taken as the addition of the 2nd accessory constituent is four mols or more -- it is -- the addition of the 2nd accessory constituent --  $0\text{mol} \leq$  -- the 2nd -- in the range which is accessory constituent  $< 4\text{ mol}$ , an elevated-temperature load life improves, moreover the outbreak of an initial IR percent defective can be reduced, so that there are many additions, and the rate of a capacity temperature change can be made small, so that there are few additions.

[0035] furthermore -- the dielectric porcelain constituent concerning this invention --  $\text{SiO}_2$  MO (however, at least one sort of elements with which M is chosen from Ba, calcium, Sr, and Mg),  $\text{Li}_2\text{O}$ , and B-2  $\text{O}_3$  from -- it is desirable to have added further the 3rd accessory constituent containing at least one sort chosen. Although this 3rd accessory constituent acts mainly as sintering acid, it also has the effectiveness of improving the percent defective of the initial insulation resistance at the time of carrying out lamination (IR). From a viewpoint of a percent-defective improvement, it is  $\text{Li}_2$ . It is more desirable to make O contain. Moreover, from a viewpoint of a percent-defective improvement, it is  $\text{SiO}$  (Srp, calcium 1-p)  $\text{J}_3$ . It is more desirable to make it contain. in this case,  $p$  --  $0.3 \leq p \leq 1$  -- it is  $0.5 \leq p \leq 1$  preferably. Although  $p$  expresses Sr atomic number, it becomes possible by making the value of this  $p$  increase to raise the rate of an excellent article of the first stage IR of it.

[0036] the ratio of said 3rd accessory constituent to 100 mols of said principal components -- oxide conversion -- it is -- zero mol --  $<$  -- the 3rd -- accessory constituent  $< 15\text{ mol}$  -- desirable --  $0.2\text{mol} \leq$  -- the 3rd -- it is accessory constituent  $\leq 6\text{ mol}$ . By making [ more ] the addition of the 3rd accessory constituent than zero mol, it is effective for an improvement of a degree of sintering, and by making an addition into less than 15 mols, decline in specific inductive capacity is suppressed and sufficient capacity can be secured.

[0037] it is desirable to have added further the 4th accessory constituent which contains the oxide (however, R -- at least one element of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) of R in the dielectric porcelain constituent concerning this invention further again. This 4th accessory constituent also has the effectiveness of improving the initial IR percent defective at the time of carrying out lamination besides [ which improves an elevated-temperature load life ] effectiveness. It is more desirable to make at least one oxide of Sc, Y, Ce, Dy, Ho, Er, Tm, Yb, and Lu contain from a viewpoint of this percent-defective improvement. the ratio of said 4th accessory constituent [ as opposed to // when adding the 4th accessory constituent / 100 mols of said principal components ] -- R conversion in an oxide -- it is --  $0.02\text{mol} \leq$  -- the 4th -- accessory constituent  $< 2\text{ mol}$  -- desirable --  $0.02\text{mol} \leq$  -- the 4th -- it is accessory constituent  $\leq 0.6\text{ mol}$ .

[0038] In addition, what is necessary is just to determine suitably terms and conditions shown in drawing 1, such as the number of laminatings of a dielectric layer 2, and thickness, according to the purpose or an application. Moreover, a dielectric layer 2 consists of a grain and a grain boundary phase, and a certain thing is [ the mean particle diameter of the grain of a dielectric layer 2 ] desirable about 1-5 micrometers. This grain boundary phase usually uses as a component the oxide of the quality of the

material which constitutes dielectric materials or an internal electrode ingredient, the oxide of the quality of the material added separately, and the oxide of the quality of the material mixed as an impurity still in process, and usually consists of glass thru/or glassiness.

[0039] Although especially the electric conduction material contained in the internal electrode layer 3 internal-electrode layer 3 is not limited, since the component of a dielectric layer 2 has reducibility-proof, base metal can be used for it. As a base metal used as electric conduction material, nickel or nickel alloy is desirable. As a nickel alloy, the alloy of one or more sorts of elements and nickel which are chosen from Mn, Cr, Co, and aluminum is desirable, and, as for nickel content in an alloy, it is desirable that it is 95 % of the weight or more. In addition, in nickel or nickel alloy, various minor constituents, such as P, Fe, and Mg, may be contained about 0.1 or less % of the weight. Although what is necessary is just to determine the thickness of an internal electrode layer suitably according to an application etc., it is usually especially desirable that it is about 1-2.5 micrometers 0.5-5 micrometers.

[0040] Although especially the electric conduction material contained in the external electrode 4 external electrode 4 is not limited, Cu, Cu alloy, nickel, nickel alloy, etc. are usually used for it. In addition, of course, Ag, an Ag-Pd alloy, etc. are usable. In addition, cheap nickel, Cu(s), and these alloys are used with this operation gestalt. Although the thickness of an external electrode should just be suitably determined according to an application etc., it is usually desirable that it is about 10-50 micrometers.

[0041] The stacked type ceramic condenser using the dielectric porcelain constituent of manufacture approach this invention of a stacked type ceramic condenser is manufactured by printing or imprinting and calcinating an external electrode, after producing the Green chip by usual print processes and the usual sheet method using a paste and calcinating this like the conventional stacked type ceramic condenser. Hereafter, the manufacture approach is explained concretely.

[0042] First, the paste for dielectric layers, the paste for internal electrodes, and the paste for external electrodes are manufactured, respectively.

[0043] The paste for paste dielectric layers for dielectric layers may be the coating of the organic system which kneaded the dielectric raw material and the organic vehicle, and may be the coating of a drainage system.

[0044] According to the presentation of the dielectric porcelain constituent concerning this invention mentioned above, the raw material which constitutes a principal component, and the raw material which constitutes the 1st - the 4th accessory constituent are used for a dielectric raw material. As a raw material which constitutes a principal component, the compound which turns into an oxide by the oxide of Sr, calcium, Ti, and Zr and/or baking is used. As a raw material which constitutes the 1st accessory constituent, one or more kinds of the single oxides or multiple oxides which are chosen from the compound which turns into these oxides are used after the oxide of V, Nb, W, Ta, and Mo, and/or baking. As a raw material which constitutes the 2nd accessory constituent, the single oxide or multiple oxide of a compound which turns into an oxide of Mn by the oxide of Mn and/or baking is used. as the raw material which constitutes the 3rd accessory constituent -- SiO<sub>2</sub> MO (however, at least one sort of elements with which M is chosen from Ba, calcium, Sr, and Mg), and Li<sub>2</sub> O and B<sub>2</sub> O<sub>3</sub> from -- at least one sort of compounds chosen are used. As a raw material which constitutes the 4th accessory constituent, the oxide (however, at least one sort as which R is chosen from Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) of R is used.

[0045] In addition, as a compound which turns into an oxide by baking, a carbonate, a nitrate, an oxalate, an organometallic compound, etc. are illustrated, for example. Of course, an oxide and the compound which turns into an oxide by baking may be used together. What is necessary is just to determine that the content of each compound in a dielectric raw material will serve as a presentation of the dielectric porcelain constituent described above after baking. As for these raw material powder, a thing with a mean particle diameter of about 0.0005-5 micrometers is usually used.

[0046] What is necessary is not to limit especially the binder that dissolves a binder into an organic solvent and is used for an organic vehicle, but just to choose it from the various usual binders, such as ethyl cellulose and a polyvinyl butyral, suitably with an organic vehicle. Moreover, what is necessary is

not to limit especially the organic solvent used at this time, either, but just to choose from organic solvents, such as a terpeneol, butyl carbitol, an acetone, and toluene, suitably according to the approaches of using, such as print processes and the sheet method.

[0047] Moreover, what is necessary is to dissolve a water-soluble binder, a dispersant, etc. in water, not to limit especially an aqueous system binder but just to choose it from polyvinyl alcohol, a cellulose, water-soluble acrylic resin, an emulsion, etc. suitably with an aqueous system coating.

[0048] The paste for internal electrodes and the paste for paste internal electrodes for external electrodes knead the various oxide used as the electrical conducting material mentioned above after the electrical conducting material which consists of various conductive metals mentioned above or an alloy, or baking, an organometallic compound, resinate, etc. and the organic vehicle mentioned above, and are prepared. Moreover, the paste for external electrodes as well as this paste for internal electrodes is prepared.

[0049] What is necessary is not to limit especially the content of the organic vehicle of each paste mentioned above, but to make the usual content, for example, a binder, and just to make a solvent into about 10 - 50 % of the weight about 1 to 5% of the weight. Moreover, during each paste, the additive chosen from various dispersants, a plasticizer, a dielectric, an insulator, etc. if needed may contain.

[0050] When using print processes, laminating printing of a dielectric paste and the paste for internal electrodes is carried out on substrates, such as polyethylene terephthalate, and after cutting in a predetermined configuration, it considers as the Green chip by exfoliating from a substrate. On the other hand, when using the sheet method, after forming a green sheet using a dielectric paste and printing an internal electrode paste on this, the laminating of these is carried out and it considers as the Green chip.

[0051] Next, it de-binder-processes and this Green chip is calcinated.

[0052] A programming rate is made in 10-100 degrees C/hour, and 5-300 degrees C/hour of 180-400 degrees C of 200-300 degrees C and the temperature holding times are more preferably made [ in / although what is necessary is just to perform debinder processing debinder processing on condition that usual, when using base metal, such as nickel and nickel alloy, as electric conduction material of an internal electrode layer especially / an air ambient atmosphere ] into 5 - 20 hours for retention temperature for 0.5 to 24 hours.

[0053] the case where base metal, such as nickel and nickel alloy, is used as electric conduction material although what is necessary is just to determine the firing environments of a baking Green chip suitably according to the class of electric conduction material under paste for internal electrode layers -- the oxygen tension of a firing environments -- desirable -- 10<sup>-10</sup> - ten to 3 Pa -- carrying out -- more -- desirable -- 10<sup>-10</sup> - it is referred to as 6x10<sup>-5</sup> to 5 Pa. If the oxygen tension at the time of baking is too low, the electric conduction material of an internal electrode will cause abnormality sintering, and will break off, and when oxygen tension is too high, there is a possibility that an internal electrode may oxidize. especially -- oxygen tension -- 10<sup>-10</sup> - by adjusting to 6x10<sup>-5</sup> to 5 Pa, it has the outstanding capacity temperature characteristic, moreover accelerated aging of insulation resistance can improve, and the dependability of the laminating mold ceramic condenser 1 obtained can be raised.

[0054] 1000-1400 degrees C of retention temperature of baking are 1200-1380 degrees C more preferably. It is because eburnation will become inadequate if retention temperature is too low, the electrode by abnormality sintering of an internal electrode will break off if retention temperature is too high, or the capacity temperature characteristic gets worse by diffusion of the internal electrode quality of the material.

[0055] It is desirable to make 200-300 degrees C /and the temperature holding time an hour for 1 to 3 hours, to make more desirable 50-500 degrees C /of 50-500 degrees C /of cooling rates in 200-300 degrees C/hour an hour more preferably an hour, for 0.5 to 8 hours, and for a firing environments to make a programming rate a reducing atmosphere as baking conditions other than this, and it is desirable to humidify and use the mixed gas of nitrogen gas and hydrogen gas as a controlled atmosphere.

[0056] When it calcinates by the reducing atmosphere, it is desirable to give annealing (heat treatment) to the sintered compact of a capacitor chip.

[0057] Annealing (heat treatment) annealing is processing for reoxidating a dielectric layer, and,

thereby, can make insulation resistance increase. 10 - 4 or more Pa of oxygen tension of an annealing ambient atmosphere is 10<sup>-1</sup>-10Pa more preferably. If oxygen tension is too low, reoxidation of a dielectric layer 2 will become difficult, and when oxygen tension is too high, there is a possibility that the internal electrode layer 3 may oxidize. It is much more effective for a defect incidence-rate improvement of initial insulation resistance (IR) by facing heat-treating the sintered compact which calcinates the dielectric porcelain constituent of this invention and is obtained especially, and adjusting oxygen tension to the range of 10<sup>-1</sup>-10Pa.

[0058] 1100 degrees C or less of retention temperature in the case of annealing are 500-1100 degrees C more preferably. When retention temperature is too low, reoxidating [ of a dielectric layer ] becomes inadequate, insulation resistance gets worse, and there is an inclination for the accelerated aging to also become short. Moreover, when retention temperature is too high, an internal electrode oxidizes, not only capacity falls, but it reacts with a dielectric base and there is an inclination for the capacity temperature characteristic, insulation resistance, and its accelerated aging to get worse. In addition, annealing can also consist of only a temperature up stroke and a temperature fall stroke. In this case, the temperature holding time is zero and retention temperature is synonymous with a maximum temperature.

[0059] It is desirable to make the temperature holding time for 6 to 10 hours, to make more desirable 50-500 degrees C /of cooling rates in 100-300 degrees C/hour an hour more preferably for 0 to 20 hours, and to humidify and use nitrogen gas as a controlled atmosphere of annealing as annealing conditions other than this, for example.

[0060] In addition, like baking mentioned above, in order to humidify nitrogen gas and mixed gas in said debinder processing and an annealing process, WETTA etc. can be used and, as for the water temperature in this case, it is desirable to consider as 5-75 degrees C.

[0061] Moreover, even if it carries out continuously, mutually-independent [ of these debinder processing, baking, and the annealing ] may be carried out, and they may be performed. It is more desirable to continue, to change an ambient atmosphere, to change an ambient atmosphere, if it calcinates by carrying out a temperature up, it cools continuously to the retention temperature in the case of baking and the retention temperature of annealing is reached, and to perform annealing treatment, without cooling after debinder processing, in performing these continuously. It is desirable to change an ambient atmosphere and to continue a temperature up further, after carrying out a temperature up under nitrogen gas or the humidified nitrogen-gas-atmosphere mind to the retention temperature at the time of debinder processing about baking on the other hand, in performing these independently, and after cooling to the retention temperature of annealing, it is desirable to change into nitrogen gas or the humidified nitrogen-gas-atmosphere mind again, and to continue cooling. Moreover, it is good also as a nitrogen-gas-atmosphere mind which could change the ambient atmosphere after carrying out a temperature up to retention temperature under nitrogen-gas-atmosphere mind about annealing, and humidified all the processes of annealing.

[0062] End-face polish is given with barrel finishing or sandblasting, it prints or imprints on the capacitor baking object acquired as mentioned above, the paste for external electrodes is calcinated on it, and the external electrode 4 is formed. As for the baking conditions of the paste for external electrodes, it is desirable to consider as 10 minutes - about 1 hour at 600-800 degrees C for example, in the mixed gas of the nitrogen gas and hydrogen gas which were humidified. And an enveloping layer (pad layer) is formed in the front face of the external electrode 4 by plating etc. if needed.

[0063] Thus, by soldering etc., the ceramic condenser 1 of this manufactured operation gestalt is mounted on a printed circuit board, and is used for various electronic equipment.

[0064] Although the operation gestalt of this invention has been explained above, as for this invention, it is needless to say that it can carry out in the mode which becomes various within limits which are not limited to such an operation gestalt at all, and do not deviate from the summary of this invention.

[0065] For example, although the stacked type ceramic condenser was illustrated as electronic parts concerning this invention with the operation gestalt mentioned above, if it has the dielectric layer which it is not limited to a stacked type ceramic condenser, but is constituted from a dielectric porcelain constituent of the above-mentioned presentation as electronic parts concerning this invention, it is good

anything.

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[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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EXAMPLE

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[Example] Next, the example which materialized the gestalt of operation of this invention more is given, and this invention is further explained to a detail. However, this invention is not limited only to these examples.

[0067] an example 1 -- the principal component raw material ( $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ) with a mean particle diameter of 0.1-1 micrometer, and the 1st - the 4th accessory constituent raw material were first prepared as a start raw material for producing dielectric materials, respectively. The oxide (the 1st accessory constituent:  $\text{V}_2\text{O}_5$  and 3rd accessory constituent:  $\text{SiO}_2 + \text{CaO}$  and 4th accessory constituent:  $\text{Y}_2\text{O}_3$ ) was used for other raw materials at the raw material of  $\text{MnO}$  using the carbonate (the 2nd accessory constituent:  $\text{MnCO}_3$ ). In addition,  $\text{SiO}_2$  which is the 3rd accessory constituent +  $\text{CaO}$  is  $\text{SiO}_2$ . And  $\text{CaSiO}_3$  obtained by carrying out wet blending of the  $\text{CaO}$  with a ball mill for 16 hours, calcinating in air at 1150 degrees C after desiccation, and carrying out wet grinding with a ball mill further for 100 hours The same property was acquired even if used.

[0068] These raw materials Empirical formula  $\{(\text{Sr}_{1-x}\text{Ca}_x)\text{O}\}_m - (\text{Ti}_{1-y}\text{Zr}_y)\text{O}_2$  (principal component) +  $\text{V}_2\text{O}_5$  (the 1st accessory constituent) +  $\text{MnCO}_3$  (the 2nd accessory constituent) + ( $\text{SiO}_2 + \text{CaO}$ ) (3rd accessory constituent) +  $\text{Y}_2\text{O}_3$  (the 4th accessory constituent) It sets. After carrying out weighing capacity so that the presentation after baking may become the compounding ratio shown in the samples 1-17 of Table 1 - 3, wet blending of these was carried out with the ball mill for about 16 hours, respectively, and the dielectric porcelain constituent (dielectric materials) was obtained by drying this.

[0069] Thus, the dielectric raw material 100 weight section after the obtained desiccation, the acrylic resin 4.8 weight section, the methylene chloride 40 weight section, the ethyl-acetate 20 weight section, the mineral spirit 6 weight section, and the acetone 4 weight section were mixed and pasted with the ball mill, and the paste for dielectric layers was obtained.

[0070] Subsequently, the nickel particle 100 weight section of 0.2-0.8 micrometers of mean diameters, the organic vehicle (what dissolved the ethyl cellulose 8 weight section in the butyl carbitol 92 weight section) 40 weight section, and the butyl carbitol 10 weight section were kneaded with 3 rolls, and were pasted, and the paste for internal electrode layers was obtained.

[0071] Subsequently, the Cu particle 100 weight section of 0.5 micrometers of mean diameters, and the organic vehicle (what dissolved the ethyl cellulose resin 8 weight section in the butyl carbitol 92 weight section) 35 weight section and the butyl carbitol 7 weight section were kneaded and pasted, and the paste for external electrodes was obtained.

[0072] Subsequently, after forming the green sheet with a thickness of 6 micrometers on the PET film using the above-mentioned paste for dielectric layers and printing the paste for internal electrode layers on this, the green sheet was exfoliated from the PET film. subsequently, these green sheets and the green sheet for protection (what does not print the paste for internal electrode layers) -- a laminating -- it was stuck by pressure and the Green chip was obtained. The number of laminatings of the sheet which has an internal electrode was made into four layers.

[0073] Subsequently, the Green chip was cut in predetermined size, debinder processing, baking, and annealing (heat treatment) were performed, and the laminating ceramic baking object was acquired.

Debinder processing was performed on condition that the air ambient atmosphere for the heating up time of 15 degrees C/hour, the retention temperature of 280 degrees C, and holding-time 8 hours. Moreover, baking is N<sub>2</sub> humidified the programming rate of 200 degrees C/hour, the retention temperature of 1200-1380 degrees C, holding-time 2 hours, and the cooling rate of 300 degrees C/hour. +H<sub>2</sub> It carried out on condition that the mixed-gas ambient atmosphere (oxygen tension is adjusted in  $2 \times 10^{-7}$  -  $5 \times 10^{-4}$  Pa). Annealing is N<sub>2</sub> humidified the retention temperature of 900 degrees C, temperature holding-time 9 hours, and the cooling rate of 300 degrees C/hour. It carried out on condition that the gas ambient atmosphere (oxygen tension is  $3.54 \times 10^{-2}$  to 2 Pa). In addition, WETTA which made water temperature 35 degrees C was used for baking and humidification of the controlled atmosphere in the case of annealing. [0074] Subsequently, N<sub>2</sub> which imprinted the paste for external electrodes to the end face, and humidified it after grinding the end face of a laminating ceramic baking object with sandblasting +H<sub>2</sub> Into the ambient atmosphere, it calcinated for 10 minutes at 800 degrees C, the external electrode was formed, and the sample of the stacked type ceramic condenser of a configuration of being shown in drawing 1 was obtained.

[0075] Thus, the size of each obtained sample was 3.2mmx1.6mmx0.6mm, the number of the dielectric layers pinched by the internal electrode layer was 4, the thickness was 4 micrometers, and the thickness of an internal electrode layer was 2 micrometers. The following property was evaluated about each sample.

[0076] Electrostatic capacity was measured with the digital LCR meter (4274made from YHP A) with the base temperature of 25 degrees C to the sample of specific inductive capacity (epsilon<sub>r</sub>) and an insulation resistance (IR) capacitor under the conditions of the frequency of 1kHz, and input signal level (measurement electrical potential difference) 1Vrms. And specific inductive capacity (with no unit) was computed from the obtained electrostatic capacity, and the electrode dimension of a capacitor sample and inter-electrode distance. Then, the insulation resistance IR after impressing DC50V to a capacitor sample for 60 seconds in 25 degrees C was measured using the insulation-resistance tester (Rby ADVANTEST CORP. 8340A), and it asked for specific resistance rho (a unit is ohmcm) by count from this measured value, and the electrode surface product of a capacitor sample and thickness. A result is shown in Table 1 - 3. As evaluation, in order to create the small capacitor of a high dielectric constant, specific-inductive-capacity epsilon<sub>r</sub> is an important property, and took 180 or more for it being more desirable and being [ 200 or more ] good. Resistivity made good more than  $1 \times 10^{12}$ -ohmcm. The value of specific-inductive-capacity epsilon<sub>r</sub> was calculated from the average of the value measured using the n= 10 sample number of capacitors. The value of specific resistance rho was made into the average of the specific resistance of ten excellent articles.

[0077] When the electrostatic capacity in the electrical potential difference of 1kHz and 1V is measured and reference temperature is made into 20 degrees C to the sample of the temperature characteristic capacitor of electrostatic capacity using an LCR meter, it investigates whether the electrostatic-capacity rate of change to temperature satisfies degree C in -2000-0 ppm /in a 20-85-degree C temperature requirement, and a result is shown in Table 1 - 3. Capacity rate-of-change \*\*C85/C20 (ppm/degree C) were computed by the following type 1.

\*\*C85/C20= {(C85-C20) /C20} x (1/65) -- Electrostatic capacity [ in / in C85 / 85 degrees C ] and C20 express the electrostatic capacity in 20 degrees C among a formula 1, however a formula 1.

[0078] Moreover, capacity rate-of-change deltaC/C in a -50 degrees C - +150 degrees C [ per typical sample 4 of this example ] temperature requirement was measured, and it graph-ized to drawing 2 . The rate of change on the basis of the capacity in 20 degrees C is expressed to this drawing. He can understand that the good capacity temperature characteristic is shown so that clearly also from this drawing.

[0079] The elevated-temperature load life was measured to the sample of an elevated-temperature load life (accelerated aging of insulation resistance) capacitor by holding in the impression condition with a direct current voltage of 8v [ /micrometer ] at 175 degrees C. This elevated-temperature load life was performed about ten capacitor samples (thickness of 4 micrometers of a dielectric layer), and was evaluated by measuring average-life time amount. A result is shown in Table 1 - 3. As evaluation, it



becomes especially important [ life ], in case an elevated-temperature load life carries out lamination of the dielectric layer, and time amount until single figure resistance falls from impression initiation was defined as the life.

[0080] Moreover, V2 in the samples 3 and 4 (all are  $m=0.985$ ) which are the examples of this invention O5 The relation between an addition (V conversion) and an elevated-temperature load lifetime was shown in drawing 3 . As shown in this drawing, when the addition of V increases and it becomes 0.2 mols, a lifetime is an average of 184 hours, and is understood that the dependability of a capacitor is higher than the time with few additions. Moreover, compared with the addition of zero mol, it has checked that a life was improved by 2000 or more times. Furthermore, V2 in the samples 9-11 (all are  $m=1.02$ ) which are the examples of this invention O5 The relation between an addition (V conversion) and an elevated-temperature load lifetime was shown in drawing 4 . As shown in this drawing, when the addition of V increases and it becomes 0.2 mols, a lifetime is before or after an average of 23 hours, and is understood that the dependability of a capacitor is higher than the time with few additions. Moreover, compared with the addition of zero mol, it has checked that a life was improved by 2000 or more times.

[0081]

[Table 1]

表1

試料 番号		第1副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性	高温負荷 寿命 (時間)
		種類	モル				$\Delta C_{85}/C_{20}$ (ppm/°C)	
1	比較例	V	0	1300	235	1E+14	-738	0.08
2	実施例	V	0.01	1300	230	1.02E+14	-710	0.2
3	実施例	V	0.1	1300	247	1.13E+14	-720	4.2
4	実施例	V	0.2	1220	240	2.84E+13	-731	184
5	実施例	V	1.8	1220	225	3E+12	-780	763
6	比較例	V	2	1220	—*	—*	—*	—*

ただし、主成分の $m=0.985$

主成分の $x=0.36$ ,  $y=0$

第2副成分( $MnO_3$ )のMn換算のモル数=0.37モル

第3副成分( $SiO_2+CaO$ )のモル数=(0.4+0.4)モル

第4副成分( $Y_2O_3$ )のY換算のモル数=0.07モル

[\*]=半導体化

[0082]

[Table 2]

表2

試料 番号		第1副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性	高温負荷 寿命 (時間)
		種類	モル				$\Delta C_{85}/C_{20}$ (ppm/°C)	
7	比較例	V	0	1380	215	2E+13	-832	<0.01
8	実施例	V	0.01	1380	223	2.5E+13	-853	0.1
9	実施例	V	0.05	1380	220	4E+13	-850	0.35
10	実施例	V	0.1	1380	230	1E+14	-880	2.3
11	実施例	V	0.2	1380	210	5E+13	-890	23
12	実施例	V	1.8	1380	212	2E+12	-908	78
13	比較例	V	2	1380	—*	—*	—*	—*

ただし、主成分の $m=1.02$

主成分の $x=0.36$ ,  $y=0$

第2副成分( $MnCO_3$ )のMn換算のモル数=0.37モル

第3副成分( $SiO_2+CaO$ )のモル数=(2.5+2.5)モル

第4副成分( $Y_2O_3$ )のY換算のモル数=0モル

[\*]=半導体化

[0083]

[Table 3]

表3

試料 番号		主成分 m	焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性 $\Delta C_{45}/C_{20}$ (ppm/°C)	高温負荷 寿命 (時間)
14	比較例	0.94	1220	—*	—*	—*	—*
15	実施例	0.985	1200	214	1E+14	-534	129
16	実施例	1.02	1380	228	2E+14	-842	2.2
17	比較例	1.08	1380	—**	—**	—**	—**

ただし、主成分の $x=0.36$ 、 $y=0$

第1副成分( $V_2O_5$ )のV換算のモル数=0.1モル

第2副成分( $MnCO_3$ )のMn換算のモル数=0.37モル

第3副成分( $SiO_2+CaO$ )のモル数=(2.5+2.5)モル

第4副成分( $Y_2O_3$ )のY換算のモル数=0.07モル

「\*」=半導体化、「\*\*」=緻密化不可

[0084] The number of mols of the 1st - the 4th accessory constituent in Table 1 - 3 is a ratio to 100 mols of principal components. Moreover, in the numeric value of specific resistance ( $\rho$ ), "mE+n" means "mx10+n" among Table 1 - 3.

[0085] From the result shown in Table 1 - 2, the following things are understood about the addition of the 1st accessory constituent. If V is not added at all like a sample 1 and a sample 7, an elevated-temperature load lifetime is extremely short. Moreover, a dielectric is semi-conductor-ized as the addition of V is two mols like a sample 6 and a sample 13, and insulation resistance is inadequate. on the other hand, with the samples 2-5 which carry out specified quantity content, and the sample of 8-12, the 1st accessory constituent Have sufficient specific inductive capacity and insulation resistance, and it is not returned in baking by reducing atmosphere. Moreover, the nickel which is an internal electrode ingredient does not oxidize, either, it can check that the dielectric porcelain constituent excellent in reducibility-proof is obtained, and the capacity temperature characteristic is excellent, and it has checked that an elevated-temperature load life (accelerated aging of insulation resistance) could moreover be improved. V2O5 It replaces with and is MoO3. WO3 Ta2 O5 And Nb2 O5 Although it added, respectively and the same conditions as the above estimated, respectively, the result with the almost same all was obtained. In addition, samples 2-5 and samples 8-12 show the example of this invention, and samples 1, 6, 7, and 13 show the example of a comparison of this invention.

[0086] From the result shown in Table 3, the following things are understood about the ratio of m of a principal component. Like a sample 14, in the case of  $m=0.94$ , the dielectric was able to be returned by baking under reducing atmosphere, and sufficient insulation resistance could not be taken, but it has checked not acting as a capacitor. Moreover, even if it carries out specified quantity content of the 1st accessory constituent to it being  $m=1.08$  like a sample 17, and it calcinates at 1380 degrees C (elevated temperature), a precise sintered compact is not obtained. In addition, samples 15 and 16 show the example of this invention, and samples 14 and 17 show the example of a comparison of this invention.

[0087]  $m=1.02$  of example 2 principal component,  $x=0.36$ ,  $y=0$ , the number of mols of the 1st accessory constituent (V) = 0.1 mols, the mol of the 3rd accessory constituent ( $SiO_2 + CaO$ ) -- a number -- = (2.5+2.5) mol and the mol of (Y) of the 4th accessory constituent -- except for having considered as =0.07 mol the number --  $MnCO_3$  as the 2nd accessory constituent The addition (Mn conversion) was changed as shown in Table 4, and it was evaluated. A result is shown in Table 4.

[0088]

[Table 4]

表4

試料 番号		第2副成分		焼成 温度 (°C)	比誘電率 $\epsilon$	比抵抗 $\rho$ ( $\Omega$ cm)	容量温度特性	高温負荷 寿命 (時間)	初期IR 不良率 (%)
		種類	モル				$\Delta C_{25}/C_{20}$ (ppm/°C)		
18	実施例	Mn	0	1380	215	8.5E+12	-610	0.02	90
19	実施例	Mn	0.05	1380	217	9.82E+12	-625	0.1	82
20	実施例	Mn	0.37	1380	226	2E+14	-841	2.2	23
21	実施例	Mn	0.73	1380	221	6.86E+13	-1238	13	10
22	実施例	Mn	1.5	1380	210	2E+13	-1676	20	7
23	実施例	Mn	3.8	1380	205	1.3E+12	-1846	32	6
24	比較例	Mn	4	1380	198	<1E+12	-1994	×	×

ただし、主成分の $m=1.02$ 主成分の $x=0.36, y=0$ 第1副成分( $V_2O_5$ )のV換算のモル数=0.1モル第3副成分( $SiO_2+CaO$ )のモル数=(2.5+2.5)モル第4副成分( $Y_2O_3$ )のY換算のモル数=0.07モル

[0089] as shown in Table 4, the addition of the 2nd accessory constituent (Mn conversion) is four mols -  
 - initial insulation resistance -- falling -- the addition of the 2nd accessory constituent -- 0mol<= -- the  
 2nd -- in the range which is accessory constituent <4 mol

\* NOTICES \*

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is the sectional view of the stacked type ceramic condenser concerning 1 operation gestalt of this invention.

[Drawing 2] Drawing 2 is a graph which shows the capacity temperature characteristic of the sample 4 which is the example of this invention.

[Drawing 3] Drawing 3 is a graph which shows the relation of the addition of V and elevated-temperature load lifetime in the samples 3 and 4 which are the examples of this invention.

[Drawing 4] Drawing 4 is a graph which shows the relation of the addition of V and elevated-temperature load lifetime in the samples 9-11 which are the examples of this invention.

[Drawing 5] Drawing 5 is a graph which shows the capacity temperature characteristic of the samples 19 and 20 which are the examples of this invention.

[Drawing 6] Drawing 6 is a graph which shows the relation between the thickness of a dielectric layer when replacing the class of the 3rd accessory constituent with, and initial insulation resistance.

[Drawing 7] Drawing 7 is a graph which shows the relation between the existence of Li addition, and the percent defective of initial insulation resistance, when the thickness of a dielectric layer is replaced with.

[Drawing 8] Drawing 8 is a graph which shows the existence of addition of Y as the 4th accessory constituent, and relation with an elevated-temperature load life.

[Drawing 9] Drawing 9 is a graph which shows the relation between the oxygen tension in a heat treatment process, and the percent defective of initial insulation resistance, when the thickness of a dielectric layer is replaced with.

[Drawing 10] drawing 10 -- SiO (Srp , calcium1-p )3 as the 3rd accessory constituent setting -- content of Sr -- it is the graph which shows relation with the rate of an excellent article of the initial insulation resistance (IR) of a capacitor sample comparatively.

[Description of Notations]

- 1 -- Stacked type ceramic condenser
- 10 -- Capacitor element body
- 2 -- Dielectric layer
- 3 -- Internal electrode layer
- 4 -- External electrode

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[Translation done.]

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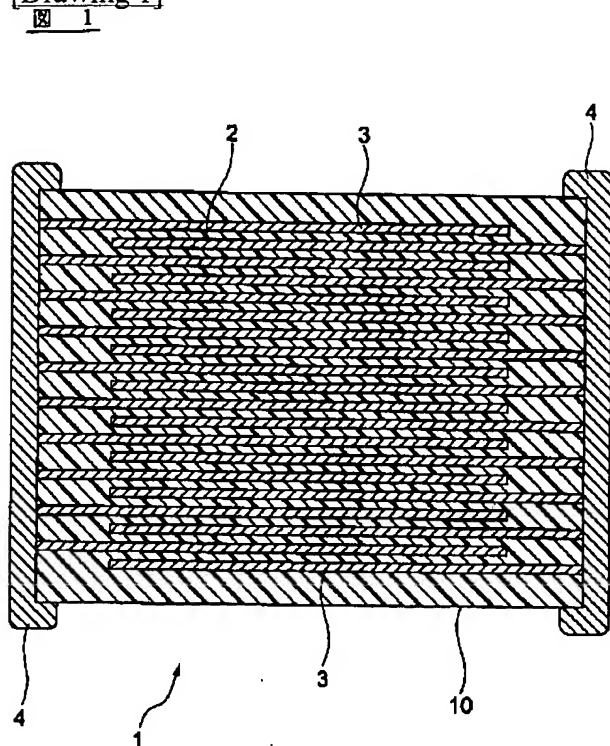
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DRAWINGS

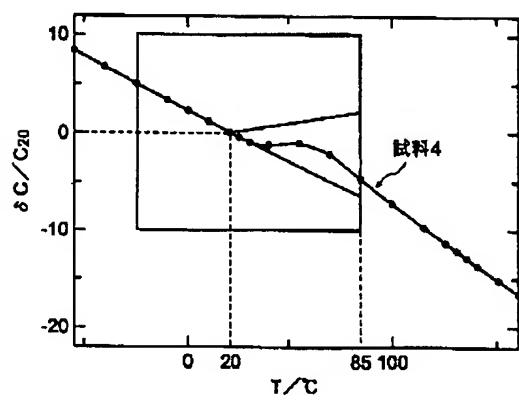
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[Drawing 1]



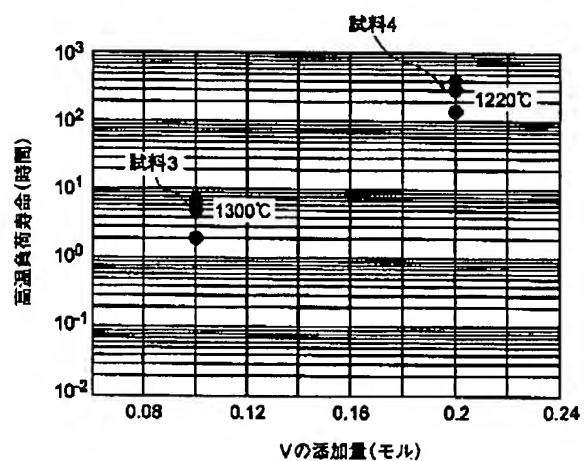
[Drawing 2]

図 2



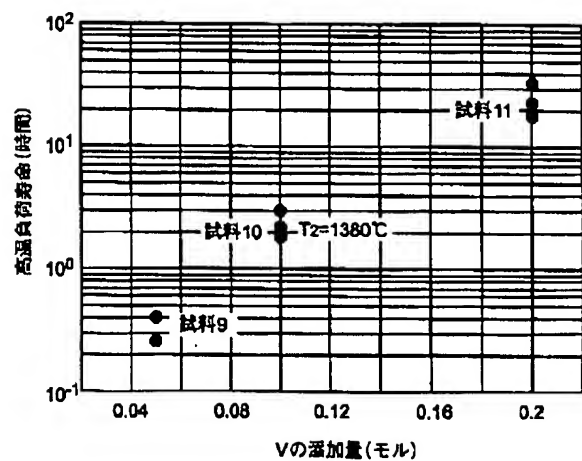
[Drawing 3]

図 3

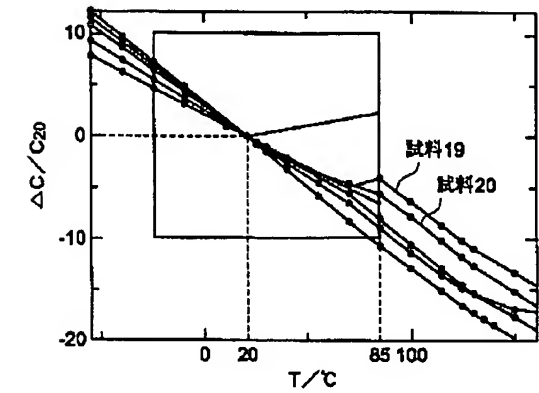


[Drawing 4]

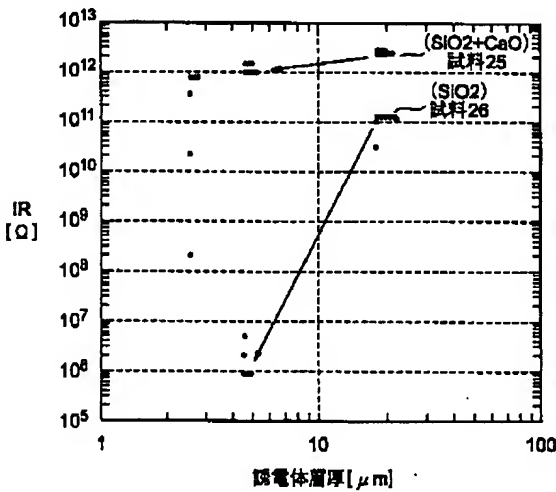
図 4



[Drawing 5]  
図 5

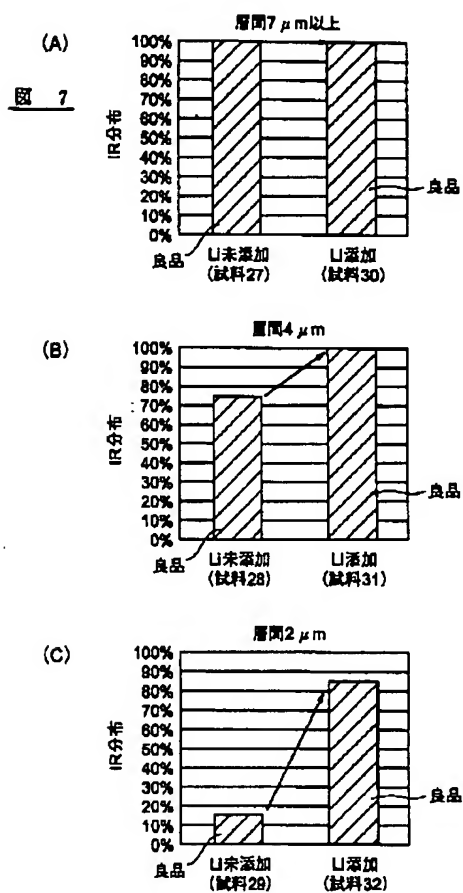


[Drawing 6]  
図 6



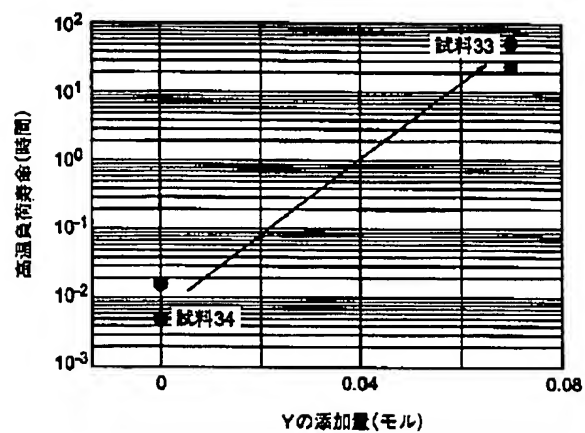
[Drawing 7]





[Drawing 8]

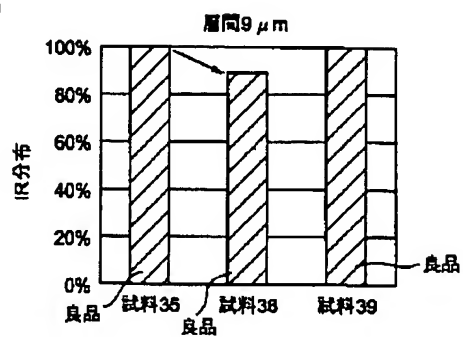
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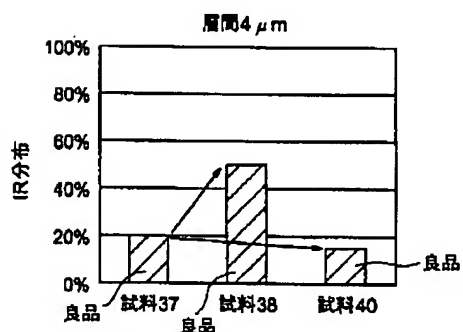
[Drawing 9]

図 9

(A)

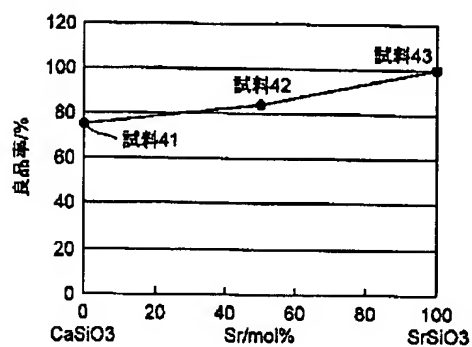


(B)



[Drawing 10]

図 10



[Translation done.]